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The amygdale minerals in the Tertiary lavas of Ireland.

III. Regional distribution.

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Summary.—Zeolites occur at most of the 670 localities studied in the Antrim Basalts, and the ten most abundant species, in order of frequency, are chabazite, thomsonite, analcime, levyne, natrolite, mesolite, stilbite, gmelinite, heulandite, and phillipsite. Gismondine, laumontite, and mordenite are recorded for the first time. Chabazite and thomsonite characterize the upper parts of the lava succession. Below, they are joined by analcime and natrolite and, in some areas where zeolitization is most intense, by stilbite and heulandite as well. These mineral zones have been mapped, and they probably reflect the temperature distribution in the lavas during zeolitization. Being discordant and clearly superimposed upon the lavas, these zones establish the late age of zeolitization in the volcanic history of Antrim. In places the zeolite zones are missing, and in their place a mineral assemblage rich in calcite, aragonite, quartz, and chalcedony is found. The tholeiite lavas that occupy a small area in north Antrim have an amygdale mineral assemblage different from that in the olivine-basalts, which constitute the remainder of the lava outcrop.

THIS paper is the third of a series dealing with the distribution of zeolites and other secondary minerals in amygdales in the Antrim Basalts. The study has been based on the examination of these minerals at some 670 localities distributed over most of the area of the basalts. The first two papers dealt with certain aspects of the distribution of the minerals; one (Walker, 1951) described the mineral zoning and distribution of chabazite crystal habit in a small area of well-exposed lavas in the east of Antrim, and the other (Walker, 1959*a*) was concerned with the peculiar distribution of gmelinite. In the present paper the regional distribution of minerals in the whole of the Antrim Basalts is discussed, and the two areas already described are located in their regional setting.

The zeolites in the Antrim Basalts have long been well known, owing largely to the work of the early nineteenth-century mineralogists.

The early work consisted mainly in the collection and description of minerals from a limited number of notable localities, and as such was reasonably complete and reliable, although the earlier workers were handicapped in their determination of the fibrous or acicular zeolites by the inadequacies of the methods then available (Hey, 1933). The work was continued in the first decades of this century by the late Robert Bell of Belfast and F. N. Ashcroft, who made extensive collections mostly from the country near Belfast. These collections are now housed in the British Museum (Natural History).

The present study was undertaken in the first place because it was suspected that the minerals were distributed in mappable zones, and it was felt that if this were so knowledge of the pattern of their distribution might help solve the difficult problem of the age and origin of zeolites in basaltic rocks. In the event, these hopes have been justified.

THE AMYGDALE MINERALS AND THEIR RELATIVE ABUNDANCE.

The list below gives the zeolites that have been identified by the writer in the Antrim Basalts. It includes some other secondary minerals, but does not include various cryptocrystalline or amorphous substances (e.g. saponite, celadonite), which are locally abundant but which have not been studied in the present investigation. Also omitted are augite and ilmenite crystals, which commonly project into amygdalae; the andradite, ilmenite, apatite, and other minerals found at Portmuck, Islandmagee (Walker, 1959*a*); and the copper minerals, which are occasionally encountered in minute quantities. Crystal cavities similar to those in the Watchung basalts, which are ascribed to anhydrite (Schaller, 1932), have been seen at one locality.

It is not easy to arrive at a reliable objective estimate of the relative abundance of the minerals. The method used here is to determine the percentage of localities at which each mineral has been identified, of the 670 localities visited in this investigation; even these figures are not fully representative, on account of the unduly large concentration of localities in some parts of the Antrim Basalts (fig. 4) where exposures are numerous, and no allowance has been made for the different relative abundance of the minerals at each locality. However it is believed that Table I gives a reasonably reliable picture of the relative abundance.

Levyne, although not usually regarded as an important mineral, is revealed as one of the more widespread of the zeolites although, on account of the usually small size of the crystals, it is rarely conspicuous. Gismondine, laumontite, and mordenite are new records for Antrim,

while the writer considers that the rather doubtful records by earlier workers of epistilbite, brewsterite, and harmotome cannot be substantiated. The list includes a probable new zeolite, related to phillipsite, for which the name 'garronite' is tentatively suggested.

TABLE I. Relative abundance of the amygdale minerals in the Tertiary lavas of Ireland.

Chabazite	...	...	...	...	...	...	...	84 % of localities
„ habit 1*	...	...	...	...	...	...	...	30
„ habit 2	...	...	...	...	...	...	...	52
„ habit 3	...	...	...	...	...	...	...	41
„ habit 4	...	...	...	...	...	...	...	19
„ habit 5	...	...	...	...	...	...	...	6
Thomsonite	...	...	...	...	...	...	...	53
Calcite †	...	...	...	...	...	...	about	40
Analcime	...	...	...	...	...	...	...	31
Levyne (and fibrous overgrowth)	...	...	...	...	...	...	...	27
Natrolite	...	...	...	...	...	...	...	23
Mesolite	...	...	...	...	...	...	...	10
Stilbite	...	...	...	...	...	...	...	9
Gmelinite	...	...	...	...	...	...	...	9
Heulandite	...	...	...	...	...	...	...	7
Phillipsite	...	...	...	...	...	...	...	6
Aragonite	...	...	...	...	...	...	...	6
Apophyllite, gyrolite	...	...	...	...	...	...	...	5
Quartz, chalcedony, opal	...	...	...	...	...	...	...	3
Gismondine	...	...	...	...	...	...	...	<1
'Garronite'	...	...	...	...	...	...	...	<1
Scolecite‡	...	...	...	...	...	...	...	<1
Laumontite	...	...	...	...	...	...	...	<1
Mordenite	...	...	...	...	...	...	...	<1
Localities with secondary minerals, but zeolites absent	...	...	...	...	...	...	...	5

* Following the chabazite habit notation of Walker (1951, p. 779).

† Calcite may originally have been much more widespread than this, much of it subsequently being dissolved away.

‡ Independent scolecite; scolecite as a thin coating on mesolite is more abundant.

The following descriptive data on the minerals are intended to supplement those given in the previous two papers of this series:

Thomsonite of faröelite habit is characteristic of the Antrim Basalts, and later bladed thomsonite of sphaerostilbite type is also widespread. Thomsonite of an unusual habit, best described as 'oolitic', occurs in two areas, one near Randalstown, and the other north of Templepatrick. The 'ooliths', pale brown in colour and individually 1 to 2 mm. in diameter, are compact spheres with radiating structure. They are grouped together either as a solid mass which may completely fill an amygdale, or as a loosely joined cluster partly or completely filling an

amygdale, or sometimes forming a bedded floor to the cavity. This 'oolitic' thomsonite is optically quite normal. A similar habit of thomsonite, with pisolith-like bodies 5 mm. in diameter is developed occasionally in tholeiite lavas at Bengore Head. Pale brown in colour, the 'pisoliths' are loosely aggregated to form a bedded floor to large amygdales, with later colourless thomsonite (of faröelite habit) and chabazite.

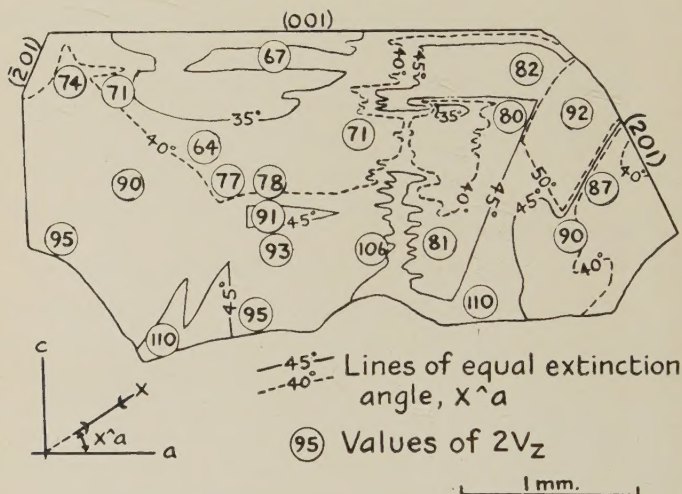


FIG. 1. Optical properties of a cleavage flake of heulandite from the Giant's Causeway area.

Stilbite forms both sheaf-like aggregates and single crystals platy parallel to $\{010\}$. All variations are found between crystals terminated by $\{110\}$ and rectangular plates of epidesmine habit terminated by $\{101\}$ alone. Unlike that in the Scottish Carboniferous basalts, the Antrim stilbite is invariably white or colourless. Optically it is monoclinic, with an extinction angle of 1 to 5° , showing sector twinning. The range of refringence observed is α 1.492–1.500, γ 1.502–1.513.

Heulandite always occurs in well-shaped crystals with little tendency to form parallel or radiating aggregates. The forms habitually present are $\{010\}$, $\{001\}$, $\{201\}$, $\{20\bar{1}\}$, and $\{110\}$ and the habit varies but little, crystals from tholeiite in north Antrim being more elongated along a than those in south Antrim, which are elongated along c . The largest crystals seen measure about 5 mm. in length, the average size being only slightly smaller than this. The Antrim heulandite is always white or colourless.

Optically the heulandite is biaxial with the acute bisectrix, γ , normal to the $\{010\}$ cleavage. The refringence covers a small range ($\alpha = 1.491$ – 1.501 ; $\beta = 1.493$ – 1.503) but the range may be almost as great as this within the confines of a single crystal, both concentric and sector zoning being developed. For example, in one crystal, β for the $\{001\}$ sector was 1.498 ; for the $\{\bar{2}01\}$ sector 1.497 ; and for a thin outer rim to both sectors 1.503 . The extinction angle and optic axial angle are similarly variable and in a single crystal each may cover a range of 30° or more. On a typical crystal from the Giant's Causeway, for instance (Fig. 1) $2V_\gamma$ covers the range 64 to 110° ; on another from south Antrim 0 to 35° . Some of these variations may be related to variations in the water content, for slight heating is sufficient to change the extinction angle markedly.

Phillipsite forms well-shaped crystals, and the Causeway tholeiites afford the best British localities for this mineral, crystals that exceptionally attain a length of 1.5 cm. being found there. Phillipsite also forms radiating aggregates, and these are especially common in the gmelinite-bearing lavas of Islandmagee and adjacent parts of east Antrim, in which phillipsite is unusual in being red in colour. Optically the Antrim phillipsite is biaxial positive, with moderate $2V$; β ranges from 1.491 to 1.499 in the specimens studied, the lower values being found in the gmelinite-bearing lavas; $\gamma - \alpha$ is of the order 0.004 .

Apophyllite shows a considerable range of crystal habit, but almost the entire range may be represented at a single quarry (fig. 3). The most characteristic habit simulates cubic symmetry, crystals being bounded by $\{100\}$ and $\{001\}$ and having the length of the $\{100\}$ faces approximately the same as the width. Small faces of $\{111\}$ are usually also present. Some crystals are clear and colourless, but usually some degree of alteration is seen, and all gradations are seen to pseudomorphs in a soft, white, greasy material.

Optically the apophyllite is sometimes uniaxial, sometimes biaxial with $2V$ up to 35° ; in some crystals both uniaxial and biaxial sectors are found, as in the example illustrated (fig. 2). Determinations of refractive index for specimens from ten localities give a range in ω of 1.532 to 1.543 . The optical sign is positive when ω lies below 1.540 , and usually negative when above. The birefringence falls with increasing refringence, as noted by Wenzel (1917), from 0.004 when $\omega = 1.532$ to less than 0.001 when ω lies above 1.540 . All samples examined with $\omega = 1.540$ or more show spectacular abnormal blue or purple polarization colours between crossed nicols due to the strong dispersion.

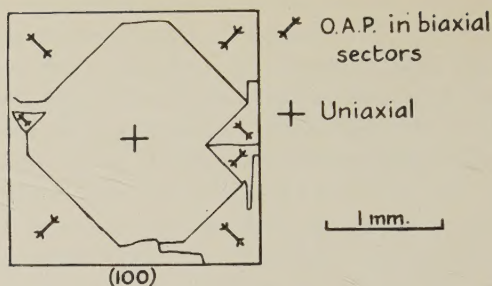


FIG. 2. Optical orientation of biaxial sectors about a uniaxial core in (001) cleavage plate of apophyllite from quarry on the north side of Carnmoney Hill.

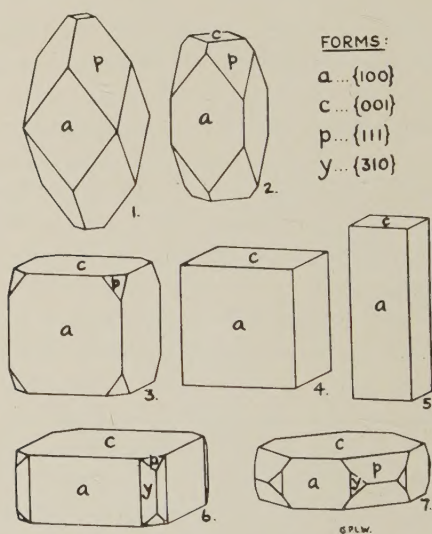


FIG. 3. Crystal habits of apophyllite encountered in a basalt quarry 1.1 mile north-east of Wolf Hill, Legoniel, Belfast. Habit 3 is most characteristic of Antrim apophyllite.

Zoned crystals normally show an increase in refringence and decrease in birefringence towards the margin, and sometimes the sign also changes. For example:

Berk Hill:	core	$\omega = 1.536$, $\epsilon - \omega = 0.003$, opt. + ;
	margin	1.543 , $\omega - \epsilon < 0.001$, - ;
Roughfort:	core	1.537 , $\epsilon - \omega = 0.002$, opt. + ;
	margin	1.542 , < 0.001 , + .

Gyrolite forms rosettes of mica-like flakes averaging 5 mm. in diameter, with pearly lustre parallel to the basal cleavage. Optically it is uniaxial negative, and measured values of ω range usually from 1.544 to 1.554, although sometimes the refractive index is appreciably lower than 1.54.

Laumontite has been found by the writer at one locality in south Antrim as prismatic crystals 5 mm. in length bounded by $\{110\}$ and $\{\bar{2}01\}$. It is in the partially dehydrated form leonhardite, and optically it is biaxial with $\alpha = 1.508$, $\gamma =$ about 1.515, $\gamma:c \{001\} 42^\circ$.

Mordenite, although identified by the writer at only two localities,¹ may be more abundant than this. It occurs in aggregates of delicate fibres and has been identified by its low refractive index.

MINERAL ASSOCIATIONS AND ZONES.

The amygdale minerals are not distributed erratically through the lavas. They are readily grouped into five mineral assemblages, as listed below. The distribution of these assemblages can be, and has been, mapped in the field, and systematic mapping shows that the assemblages characterize definite zones. It should be pointed out at the outset, however, that the amygdale minerals in the tholeiite lavas of north Antrim do not fit into this scheme, and the present discussion applies only to the olivine-basalt lavas, which constitute the greater part of the Antrim lava pile.

The five mineral assemblages are as follows:

Stilbite-heulandite assemblage; essential minerals stilbite and heulandite. They may be associated with any of the other zeolites, gmelinite excepted. The most common associates are chabazite, calcite, analcime, and natrolite; thomsonite, apophyllite, and gyrolite also commonly occur.

Analcime-natrolite assemblage; essential minerals analcime or natrolite or both in the absence of stilbite, heulandite, and gmelinite. The most common associates are chabazite and calcite; apophyllite and gyrolite, and sometimes phillipsite and levyne may also be present.

Chabazite-thomsonite assemblage; characterized by the association of chabazite and thomsonite in the absence of gmelinite and of the index minerals of the two preceding assemblages. Levyne usually occurs as well, and associated minerals include phillipsite, calcite, and less commonly apophyllite and gyrolite.

Gmelinite assemblage; the essential feature is the presence of gmelinite,

¹ In a quarry $\frac{1}{2}$ mile N.N.E. of summit of White Mountain; and in a shore exposure at Blackcave, Islandmagee

with which may be associated any of the other zeolites (in practice stilbite and heulandite are missing). The common associates are chabazite, thomsonite, analcime, phillipsite, levyne, calcite, and aragonite.

Plumose-calcite-aragonite-quartz assemblage; quartz, chalcedony, and opal are confined to this assemblage, and aragonite is much more abundant here than elsewhere. The calcite possesses a distinctive 'plumose' habit not found elsewhere, and $\{02\bar{2}1\}$ is the dominant form. Typically zeolites are completely absent, but there is a transitional assemblage in which zeolites are associated with an abundance of calcite, aragonite, and quartz.

The distribution of these five mineral assemblages is represented on the map, fig. 5. This map is based on data from 670 localities, and the degree of control achieved in locating the zone boundaries may be seen by comparison with the locality map, fig. 4. The chabazite-thomsonite assemblage is to be regarded as the most characteristic of the Antrim Basalt, for it covers the largest area and probably constitutes more than half of the volume of the lavas. It is followed downwards by the analcime-natrolite assemblage which, although covering a rather small area on the map, probably underlies the chabazite-thomsonite zone as a more or less continuous zone over most of the area of the basalts and may constitute nearly half of the total volume.

The distribution of the chabazite-thomsonite and analcime-natrolite assemblages.

The first clear picture of the distribution of the mineral assemblages was obtained by a detailed study of the well-exposed ground of the Garron Plateau and adjacent areas in eastern Antrim (Walker, 1951). Two assemblages are developed there, namely the analcime-natrolite assemblage, which almost everywhere forms a zone in the lower few hundred feet of the lava succession, and the chabazite-thomsonite assemblage, which everywhere overlies it and in a few places underlies it as well. Although conforming roughly to the stratification of the lavas, when examined in detail the zeolite zones are seen to be discordant and the same applies to the chabazite crystal habit zones that were mapped; this indicates clearly that the zeolites postdate the lavas in which they occur by a substantial margin.

It is clear that the general relations worked out in the Garron area apply to the greater part of the Antrim Basalts. An analcime-natrolite zone has been mapped around most of the periphery of the basalt plateau (fig. 5) and in places it is seen as small inliers within the plateau.

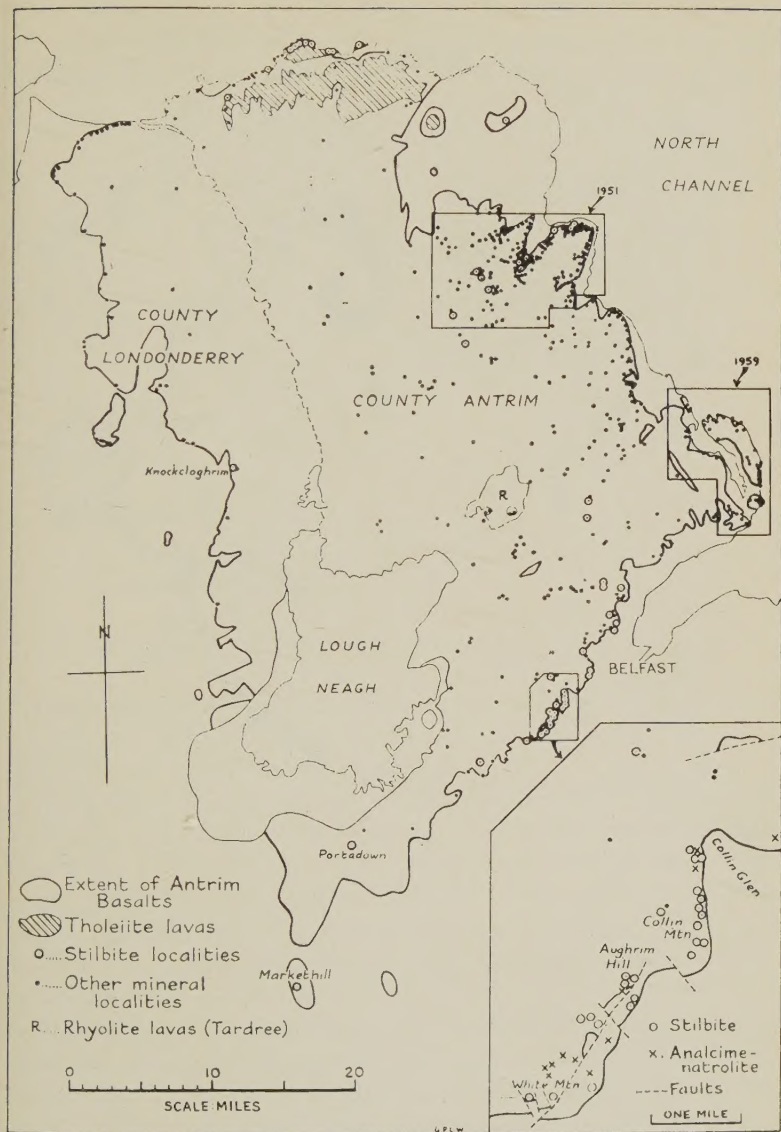


FIG. 4. Map of the Antrim Basalts showing the localities on which the zeolite distribution map is based, and also showing the distribution of stilbite. Detailed maps of the areas labelled '1951' and '1959' have been published in the two earlier papers of this series.

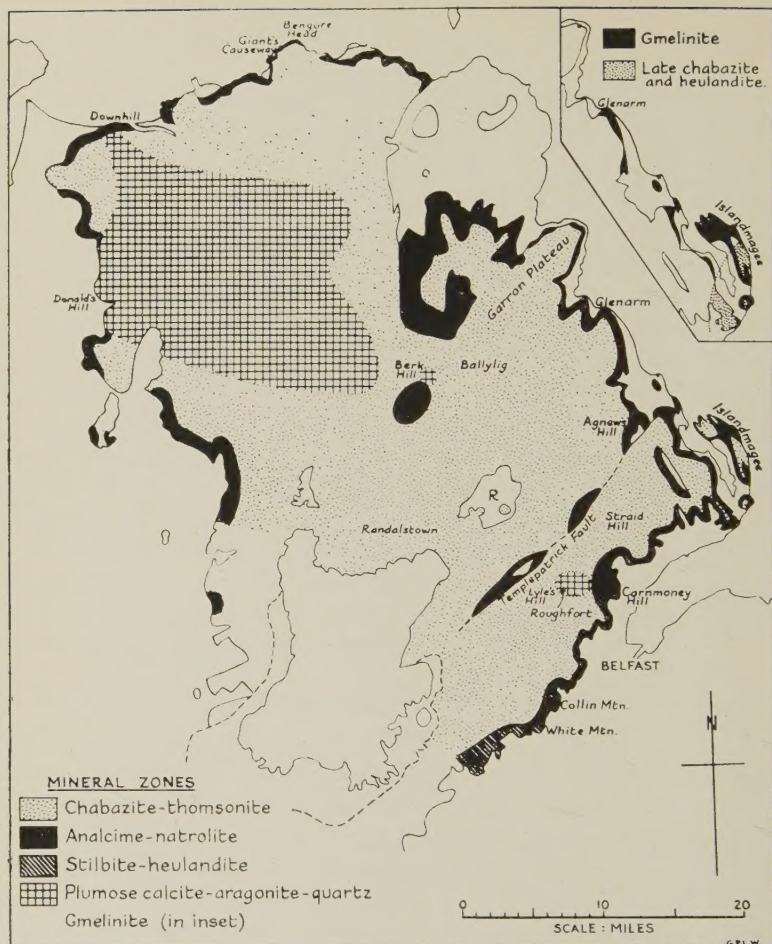


FIG. 5. Zeolite distribution map of the Antrim Basalts.

Inliers of the zone are also found along the northern, upthrow, side of the Templepatrick fault, where the lower parts of the basalt pile have been brought to the surface by faulting. Everywhere the zone is overlain by one with the chabazite-thomsonite assemblage.

Although mapped as part of the same zone, and clearly requiring closely similar conditions for their formation, there is a tendency for analcime and natrolite to be mutually exclusive or antipathetic to the extent that when one is abundant the other usually is not. Analcime

is predominant along the north coast from Downhill to the Causeway (fig. 6); along the north and east of the Garron Plateau to as far south as Carnlough; and in south Antrim south-westwards from Belfast.

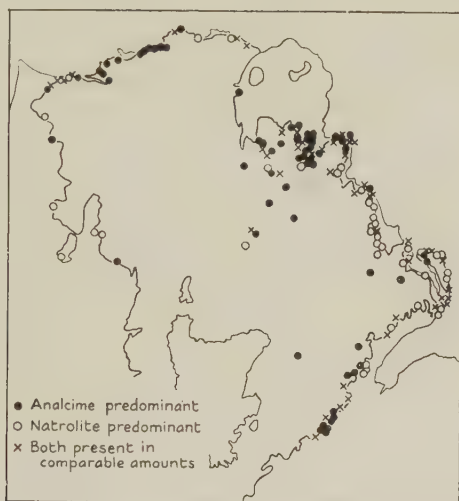


FIG. 6. The distribution of analcime and natrolite in the analcime natrolite zone.

Natrolite is predominant in eastern Antrim at most localities from Carnlough to Belfast; along the north coast near Whitepark Bay and at Downhill; and in the west near Carntogher.

The distribution of chabazite crystal habits likewise shows everywhere a general pattern similar to that worked out for the Garron area, although exposures are seldom sufficiently numerous to enable a habit distribution map to be drawn. In the Garron Plateau and elsewhere those localities bearing chabazite crystals of more complex habit (habits 4 and 5, Walker, 1951) have a distribution very similar to that of the analcime-natrolite zone, being found in the lower few hundred feet of the lavas and distributed around the periphery of the basalt outcrop; these complex habits are also seen in a few inliers, such as that of Berk Hill and the ground to the north. The crystal habit of chabazite changes progressively upwards and crystals of the simplest habits (1 and 2) are characteristic of the higher parts of the basalt pile, for example, Agnew's Hill and the higher parts of the Garron Plateau.

Herschelite (chabazite of phacolite habit with {0001} developed) has been found at a single locality low down in the basalts, a path exposure

in a slip on the basalt escarpment $\frac{1}{2}$ mile south of Drumnageagh House, south-east of Glenarm. The herschelite is associated with chabazite of lower habits (3 or 4) and a little later chabazite of habit 2, together with natrolite.

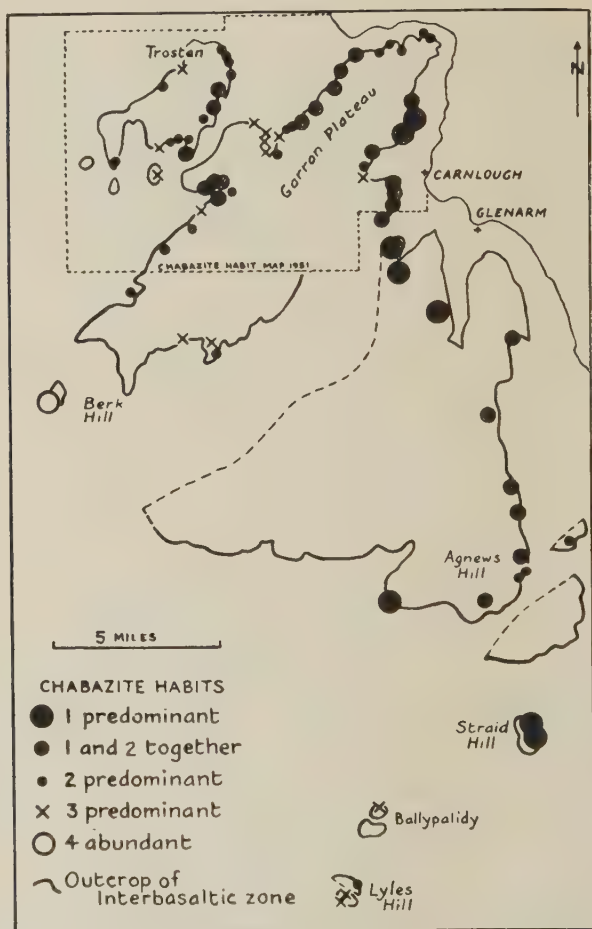


FIG. 7. The crystal habit of chabazite in lavas at the base of the Upper Basalts, eastern Antrim.

In eastern Antrim there is a tendency for the chabazite 'isohabit surfaces'¹ to rise westwards or south-westwards through the lavas.

¹ The term 'isohabit' was suggested in the 1951 paper for lines of equal crystal habit as drawn on a map of the Carron Plateau area.

Thus, if one takes a recognizable stratigraphic horizon, the base of the Upper Basalts (fig. 7), habits 1 and 2 are the only habits found at this level in the east of the region (the eastern part of the Garron Plateau; the areas near Carnlough; Glenarm; Scawt Hill; Agnew's Hill; and Straid Hill), while habits 4 and 5 are found in the west (Trostan; Ballylig; Berk Hill; Ballypalidy; and Lyle's Hill). The higher habits are not found at all in the basalts farther east.

The distribution of stilbite and heulandite.

Where the analcime-natrolite zone near the base of the lavas is thickest, these two minerals are joined by stilbite and heulandite; where these latter minerals are abundant there is justification for the recognition of a separate mineral assemblage, the stilbite-heulandite assemblage. This assemblage is well developed only in the south of Antrim, along the escarpment south-westwards from Belfast, and is best seen in that stretch from Collin Glen to the White Mountain (figs. 4 and 5). There are a few exposures farther towards the south-west (Maghaberry, Portadown, and Markethill) that also contain stilbite or heulandite, but exposures are too scattered to be certain that the stilbite-heulandite zone extends continuously in that direction.

In the stretch from Collin Glen to White Mountain, stilbite and heulandite are extremely abundant in a number of quarries in the lower 400 feet of lavas, and they are accompanied by chabazite, often of habits 3 and 4, analcime, natrolite, and by much calcite, often brown. These minerals are usually found in the red weathered amygdaloidal top and base of a lava flow, while other minerals, namely thomsonite, chabazite, apophyllite, and gyrolite are met with in the less abundant amygdales in the fresh interior of the flow (see p. 522). Thomsonite, although common, is almost never found associated with stilbite or heulandite in the same amygdale; these minerals are segregated in different parts of the same lava flow. Likewise it is extremely rare for apophyllite or gyrolite to appear in the same cavity as stilbite or heulandite.

The age relations of the minerals are in some doubt. Heulandite, when associated with stilbite, is usually found as small, well-shaped crystals around the walls of the cavity, embedded in stilbite, which mineral is thus probably later. The most common associate of stilbite is chabazite of habit 2 to 3. Sometimes the chabazite crystals have been deposited on the stilbite, and sometimes the reverse is true, but more often there is no reliable indication of the relative age and it seems as though the two minerals have crystallized more or less simultaneously,

or their periods of crystallization have overlapped. Analcime is invariably later than stilbite.

While exposures in the stilbite-heulandite zone of the area around White Mountain and Collin Glen are generally excellent, they fail at critical points, and the shape of the zone is not certain. Exposures are not sufficiently good to establish that the stilbite-heulandite zone is flat-lying and does not cut steeply across the lava stratification, and the main evidence favouring the former arrangement is the restriction of stilbite and heulandite to a very narrow belt, nowhere more than a mile in width, along the basalt escarpment where the lower parts of the lava succession are exposed.

If one assumes, then, that the zone is flat-lying, it must attain its greatest known thickness, around 400 feet, on Collin Mountain. On the White Mountain the thickness has probably decreased to around 100 feet. There is an indication that the stilbite-heulandite assemblage is underlain and overlain by a narrow zone characterized by analcime and natrolite and that the former zone forms in fact the core of the analcime-natrolite zone. Traced north-eastwards towards Belfast it passes into the typical natrolite-analcime assemblage, with sporadic stilbite or heulandite in small amount.

The great bulk of the stilbite and heulandite in Antrim is in the region of White Mountain and Collin Glen, and there is no comparable zone elsewhere. Stilbite occurs sparsely at a number of localities on the edge of, or near, the Garron Plateau (fig. 4), most of them in the Lower Basalts near their base (e.g. in Glenariff Glen) within the analcime-natrolite zone. Stilbite is abundant at a large quarry at Knockcloughrim at the western edge of the basalt outcrop; heulandite is sparsely developed at Portballintrae on the north coast; and stilbite is seen on the upthrow side of the Templepatrick fault, near the base of the lavas at Ballyclare.

At one locality in the stilbite-heulandite zone, a quarry $\frac{1}{4}$ mile north-west of Castle Robin and $\frac{3}{4}$ mile north-east of the White Mountain, crystal cavities several centimetres in length were found in large amygdaloids with later analcime growing in the cavities. The shape, although unlike that of calcite, is not sufficiently well-defined to enable positive identification of the mineral leached out. The general characters remind one of the cavities due to anhydrite in the Watchung basalts (Schaller, 1932). Laumontite (leonhardite) has been observed at one locality in the stilbite-heulandite zone (Belshaw's Quarry, one mile south-west of the White Mountain) in small amount in the lowest lava flow, associated with chabazite, stilbite, and heulandite.

The distribution of apophyllite and gyrolite.

Apophyllite and gyrolite, a pair of minerals seldom seen apart, have been found at some thirty localities (fig. 8). Most are in the south-east of Antrim, especially near Belfast and in the White Mountain area, and



FIG. 8. The distribution of apophyllite and gyrolite in the Antrim Basalts.

the most important are: *Belfast area*: Quarries on Catcairn and Wolf Hill; on the northern and western side of Carnmoney Hill (one described by Fleischmann, 1910); abandoned quarries (Fleischmann, 1910) at Ballyhenry; *White Mountain area*: abundant gyrolite in quarries near Castlerobin; sparse apophyllite in quarry north-west of summit of Collin Mountain; *Other areas*: Quarries in Upper Basalts, Berk Hill.

Very fine collections of apophyllite from quarries near Belfast were made by the late Robert Bell and F. N. Ashcroft in the first decades of this century. They include the best British examples of the mineral, the crystals commonly exceeding 1 cm. in size. Apophyllite and gyrolite are virtually confined to the often very large and horizontally flattened cavities in the black interior of massive basalt lava flows, and as such cavities are seldom numerous and the fresh basalt is very tough good specimens can in practice be obtained only in quarries that are actively worked.

Specimens from these localities have a markedly uniform appearance. The cavities have a compact radiating-fibrous lining of faröelite, and

apophyllite forms well-shaped crystals, sometimes water-clear, at other times dull white, resting on it. Closely associated, and also later than the faröelite, are rosettes of pearly-white leaves of gyrolite, and little sheaves and tufts of thomsonite of sphaerostilbite habit or, less commonly, thomsonite in radiating clusters of separate needles or fibres. Sometimes there are tiny brown crystals of calcite as well. Adjacent cavities may contain faröelite, levyne, or chabazite.

Apophyllite is invariably later than thomsonite of faröelite habit; the age relationship to the other zeolites is seldom apparent but several examples have been found of apophyllite following chabazite and stilbite, and one with small crystals of apophyllite encrusting analcime.

Apophyllite and gyrolite have been found in the stilbite-heulandite, analcime-natrolite, and chabazite-thomsonite assemblages, most of the localities being in the south-east of Antrim. Before considering the possible zonal distribution, however, one must take account of the following significant observations:

With two exceptions, apophyllite and gyrolite have been encountered only in quarries; they are practically confined to the massive black interior of lava flows, being very rare in the red amygdaloidal tops; and apophyllite is manifestly one of the least stable of the minerals, the water-clear crystals readily becoming white and chalky on weathering (cf. Bailey, 1941).

These observations are interpreted as meaning that apophyllite is readily destroyed by weathering and the known distribution may bear little or no relationship to the actual distribution just below the zone of surface weathering; apophyllite has been destroyed in practically all natural exposures and is seen only where quarries reach below the surface zone of weathering, as in the quarries that are so numerous in south-east Antrim. Even in these quarries apophyllite may have been destroyed in the more permeable red amygdaloidal tops of the lava flows, for it is now seen only in the massive interior of the flows.

The distribution of gmelinite.

Gmelinite is restricted to a narrow zone along the eastern seaboard of Antrim in which it is extremely abundant. Its distribution has already been described and discussed (Walker, 1959a).

The distribution of the calcite-aragonite-quartz assemblage.

The variety of calcite referred to in this paper as 'plumose' forms more or less radiating aggregates of crystals with curved cleavage

surfaces, and the crystals have grown in the direction of one of the Miller crystallographic axes, with two cleavages disposed approximately normal to the rock-surface from which the calcite grew. Plumose calcite occurs over a large and well-defined area in the north-west of the basalt outcrop as an important mineral in a well-defined mineral assemblage. In it the calcite is characteristically associated with aragonite and commonly with quartz, chalcedony, opal, and macroscopic chlorite; usually calcite of normal habit and sometimes pisolitic calcite and 'satin spar' (fibrous calcite) are also present. Zeolites are completely absent.

The plumose calcite is often pale green in colour, and usually cloudy or milky. Curved crystal faces are often seen terminating crystals in the aggregates; these faces are seldom bright, but it is clear that {02 $\bar{2}$ 1} is the predominant and often the only form developed. Quite commonly normal calcite, clear and colourless and with plane cleavage surfaces, continues the growth of the plumose calcite as a parallel overgrowth.

Aragonite typically forms solid radiating columnar aggregates filling joints and amygdales, and exceptionally the individuals in these aggregates attain a length of over one foot. Aragonite in these aggregates is often pale pink or lilac in colour. Frequently it is largely or entirely replaced by a sugar-grained aggregate of calcite, the radiating form of the original mineral being preserved in the paramorphs.

Very rarely delicate acicular crystals of aragonite are encountered as, for instance, in a basalt quarry 2 miles SSE. of Donald's Hill. The basalt here contains cavities up to a foot or more in diameter, which are lined with a layer half an inch thick of green plumose calcite, superficially very like prehnite. This is succeeded by a layer of chalcedony, and that in turn by quartz, and the slender prisms of aragonite occur in cavities in the quartz, accompanied by a little normal calcite.

Quartz and chalcedony, apart from their occurrence in tholeiites in north Antrim, are practically confined in the Antrim Basalts to the plumose-calcite zone. In this zone they are both abundant, and are sometimes accompanied by a little milky or hyaline opal. These minerals are later than the bulk of the calcite.

This assemblage of minerals is present over a large area of lavas in the north of County Londonderry and adjacent parts of Antrim. The boundaries of this zone are fairly reliably localized along the western escarpment in Co. Londonderry, but elsewhere exposures are not sufficiently abundant to enable this to be done; no exposures have, for example, been found in the broad and low-lying valley of the river Bann, which crosses the outcrop of the zone. Around the margins of the

plumose-calcite-aragonite-quartz zone, from which zeolites are absent, a transitional zone is found in which the minerals are accompanied by zeolites. The arm of the zone shown on the map, fig. 5, extending towards the north coast near Downhill is inferred from the abundance of carbonates in the zeolite-bearing assemblages on the coast there.

An assemblage of minerals similar to that of the plumose-calcite zone is seen at a single quarry north of Ballymena, just east of the Berk Hill outlier, and at a number of quarries near the hamlet of Roughfort, east of Templepatrick, in south Antrim.

The three-dimensional shape of the plumose-calcite zone is not known, mainly on account of the shortage of suitable exposures. The characteristic mineral assemblage of the zone is certainly developed through a vertical thickness of up to 500 feet of lavas, and nowhere has evidence been found of its being underlain or overlain by zeolite-bearing zones. The origin is likewise uncertain. The arguments that show that formation of zeolites took place long after the exposed lavas had been erupted apply with equal force here. One can envisage the minerals being formed at a late stage in the volcanic history of the area by regional thermal waters perhaps rising from some deep-seated source but there is no indication of what that source might be.

In the Tertiary lava region of eastern Iceland a very similar mineral assemblage is encountered in the vicinity of major volcanic centres; there the calcite, aragonite, quartz, and other minerals, are clearly due to heated solutions or gases coming from those centres and permeating the adjacent lavas. It is tempting to see in the plumose-calcite-aragonite-quartz zone of the Antrim Basalts evidence of a comparable Tertiary volcanic centre. However, the available geological evidence is opposed to such a possibility (p. 525).

MINERALS IN THE CAUSEWAY THOLEIITES.

In the Antrim Basalts tholeiite lavas are confined to the coastal strip along the north of Antrim, where there is a group of thick flows with a maximum aggregate thickness of about 450 feet (Tomkeieff, 1940; Patterson, 1955). The group, referred to in the older literature as the 'Upper Basalts', was renamed the Middle Basalts by Patterson who showed that they were underlain and overlain by olivine-basalts (the Lower and Upper Basalts of Patterson), the former ranging in thickness from 300 feet near Ballycastle and Portrush to less than 100 feet near Carrickarade. The uppermost part of the Lower Basalts had suffered deep lateritic weathering prior to the eruption of the tholeiite flows.

The tholeiite lavas are famous for their columnar jointing, and are well exposed in the coastal cliffs from the Giant's Causeway to Bengore Head. These cliffs, up to 360 feet high, are accessible by cliff-path, and the screes from them contain very fine specimens of the amygdale-minerals; other localities from which mineral specimens may be obtained from the tholeiites include Craigahulliar quarry, near Portrush, and, according to the literature, Rathlin Island. The Giant's Causeway is often given as a mineral locality in the literature although, as Ashcroft (1916) has pointed out, the term 'Giant's Causeway' was often used in the widest sense to indicate almost any locality along the north coast of Antrim.

The following is a list of the minerals recorded in the literature, probably from tholeiite lavas, in the Causeway area: analcime, apophyllite, brewsterite, chabazite, harmotome, heulandite, mesolite, phillipsite, scolecite, stilbite, and thomsonite.

The writer has not found apophyllite, brewsterite, or harmotome, and suspects that chabazite was mis-identified as apophyllite, phillipsite as harmotome (these two minerals being indistinguishable in the hand-specimen), and stilbite as brewsterite; stilbite resembles brewsterite very closely when terminated by $\{10\bar{1}\}$ alone. To the list can now be added levyne, which although rare does undoubtedly occur, together with the fibrous overgrowth that is so characteristic of much of the Antrim levyne; also natrolite, opal, and celadonite; and possibly laumontite.

The tholeiite lavas, like the olivine-basalts, generally have amygdales in the upper half or third of the flow, culminating in a highly amygdaloidal red topmost part, but the amygdale-minerals exhibit certain differences when compared with those in the olivine-basalts. The first difference is the presence of celadonite, a dark green mineraloid that is confined to the tholeiites. It forms amygdale-linings in the interior of a flow below its red top. When this lining weathers, the amygdales separate from the basalt and resemble almonds much more closely than they ever do in the olivine-basalts, where amygdale and basalt are firmly knit together. Occasional cavities in the tholeiites are completely filled with celadonite.

A second distinctive character is the abundance of quartz, chalcedony, and opal in the tholeiites. Outside the plumose-calcite zone, these silica minerals are almost never encountered in the olivine-basalts. Thirdly, stilbite and heulandite have a rather different habit in the tholeiite lavas. Stilbite is in small crystals with square cross-section or in

hemispherical aggregates with smooth outer surface, and is usually terminated by $\{10\bar{1}\}$ alone; in the olivine-basalts it is in large, platy crystals or in large sheaf-like aggregates more commonly terminated by $\{110\}$. Heulandite in the tholeiites is generally more elongated parallel to a than in the olivine-basalts.

A marked difference in the assemblage of amygdale minerals is found in the two types of basalt where they are contiguous, as in the Causeway cliffs. The olivine-basalts bear chabazite, analcime, natrolite, and calcite, with only traces of other minerals. The overlying tholeiites contain in addition to these minerals an abundance of stilbite, heulandite, and phillipsite at most localities, as well as celadonite and silica minerals. Indeed, one can quite reliably map the two basalt types solely on the basis of their secondary minerals. This is the only known instance in the Antrim Basalts where the composition of the lava obviously exercises a control on the mineral assemblage formed. A similar relationship is known in other areas, for instance in Iceland and Mozambique (Holmes, 1916).

A form of zonal arrangement of amygdale-minerals within the confines of a single lava flow is often observed in olivine-basalts with, for instance, thomsonite confined to the fresh interior of a flow and stilbite and heulandite to the red amygdaloidal top (p. 515). Such zoning reflects the different permeability of the massive interior of a flow and the slaggy top. In the tholeiite flows a zonal arrangement is nearly always present, with chalcedony and quartz confined to the black interior and zeolites confined to the more highly vesicular upper parts.

Occasionally a much more striking zoning is seen in the tholeiites. Careful examination of fallen blocks on the western side of Benanouran Head reveals the following zonal arrangement in a single lava flow:

Red decomposed amygdaloidal top: much calcite, chabazite.

Rather decomposed amygdaloidal basalt below red top: chabazite and phillipsite.

Interior of flow (upper part), with few cavities, horizontally flattened by flow: celadonite, stilbite, heulandite, chabazite, and phillipsite.

Chabazite and phillipsite are both probably absent from the lower part of this zone.

Interior of flow, sparse cavities, horizontally flattened by flow: celadonite, chalcedony, quartz, opal; zeolites absent.

Lower half of flow, free from cavities: amygdale-minerals absent.

It was at first thought that this zonal arrangement might be due to mineralization during the cooling of the flow on the surface, but this

idea was abandoned in face of the overwhelming evidence that in general zeolitization is later. It is more probably related to the progressive upward increase in porosity and permeability of the basalt.

ZEOLITES IN DOLERITE INTRUSIONS.

Numerous dolerite intrusions—dykes, plugs, and sills—are found associated with the lavas. Most are of olivine-dolerite or crinanite, similar in composition to the lavas, and of the same general age. The dolerites usually contain zeolites, often forming around 5 per cent. of the volume of the rock. The zeolites occupy interstitial patches between the pyrogenetic minerals, and to a certain extent they replace these minerals; in some dolerites zeolites are also found filling small amygdalae in the rock. Dolerite pegmatites are generally richer in zeolites than the main dolerite body in which they occur.

The zeolites in the several dolerite intrusions that have been studied by the writer are similar to those in the adjacent lavas, which comprise the country rock. Those intrusions in the lower parts of the lava pile and in the subjacent sedimentary rocks contain an assemblage of zeolites that includes prominent analcime or natrolite. Intrusions high in the lava pile lack analcime and natrolite and bear the minerals typical of the chabazite-thomsonite assemblage. Thus the Parkgate plug (Walker, 1959*b*) contains an abundance of levyne, together with chabazite and phillipsite, and the dolerite is locally veined by thomsonite and chabazite; the Ticloy plug contains phillipsite, chabazite, rare levyne, and a little probable analcime; and the Donegore 'dyke' bears levyne and thomsonite. All three plugs cut lavas in which the thomsonite-chabazite assemblage is developed. The conclusion appears inescapable that zeolites in dolerites and in the country rock were formed at one and the same time.

DISCUSSION.

Perhaps the main result of this work has been to show that the distribution of amygdale-minerals is orderly and capable of being mapped; that the minerals occur in zones that are mostly flat-lying and nearly parallel to the stratification of the lavas, but in detail are seen to be discordant. All the evidence indicates that zeolitization took place at a time probably long subsequent to the eruption of the individual lava flows in which the minerals occur, and after at least 1 000 feet of lavas had been erupted, and locally it is possible to relate the period of zeolitization to the period of main movement along faults (Walker,

1951 and 1959a). There seems no direct means at present of determining in Antrim how much of the lava pile has subsequently been eroded away, but in Iceland, where the zeolite zones are broadly similar to those in Antrim, there is evidence that the original top of the lava pile stood some 2 000 feet above the top of the analcime zone. If this were so in Antrim it would indicate an original thickness of about 2 500 feet for the lavas in most of eastern Antrim, as compared with the present maximum exposed thickness of about 1 000 feet.

It seems possible to group the secondary mineral zones of the olivine-basalts into two categories: the normal zones, which are regional in extent and which are nearly parallel to the lava stratification; and the local zones, which are markedly discordant and of limited distribution. Into the first category come the zones of the Garron Plateau area and their extension elsewhere; into the second come the gmelinite zone and the plumose-calcite-aragonite-quartz zone.

The normal zoning consists of a chabazite-thomsonite assemblage underlain by one in which chabazite and thomsonite are joined by analcime and natrolite. In some places these minerals in the lower zone are joined by stilbite and heulandite, and where sufficiently abundant a distinct stilbite-heulandite zone may be distinguished. Broadly, the intensity of zeolitization increases as the number of mineral species present increases, and it is believed that these zones reflect a temperature control, the most intense zeolitization and highest temperature being attained in the stilbite-heulandite zone. It is possible that the flat-lying nature of the zones may be due to their being roughly parallel to the original top of the lava pile at the time when zeolitization was taking place; in any case it is to be expected in a pile of lava flows that are characteristically extremely permeable laterally along the slaggy tops of the flows but relatively impermeable in a direction normal to the stratification.

The writer considers that zeolitization got under way only after a certain critical thickness of lavas had accumulated, the blanketing effect of the upper lavas permitting the required build-up of heat in the lower flows. Antrim supplies no data on the value of this critical thickness, but Icelandic experience suggests that it may be of the order of 500 to 1 000 feet. Zeolitization took place in waterlogged basalt in which the water was of meteoric origin. The heat required came partly from below, and partly from exothermic hydration reactions, including the hydration of olivine, in the basalts; substantial increments also came from dykes and other bodies intruded into the lavas. Some of the faults cutting the

Garron Plateau (Walker, 1951, p. 788) apparently allowed heat to escape, and adjacent to them the higher-temperature analcime-natrolite assemblage is missing owing to this loss of heat.

The abnormal zoning is more difficult of explanation, and one must search for geological clues to account for it. The gmelinite zone has been shown to approximate in its position to a major fault zone, and it is reasonable to suspect a genetic connexion between the two, although it is difficult to account for the absence of gmelinite in close proximity to many another fault cutting lavas in Antrim and elsewhere. The agency of heated waters rising from depth may be responsible, but there are other possibilities. One is that the lavas containing gmelinite may have suffered an incursion of sea water during zeolitization, in place of the more usual meteoric waters. Geological evidence does no more than leave open the possibility that incursion of sea water may have been consequent on the downwarping of the lavas in the Islandmagee fault zone before or during faulting. It is for future experimental work to show whether the presence of chlorides in solution promotes crystallization of gmelinite or not, and whether sea water is responsible for the distinctive pink or red coloration of the gmelinite and other minerals in the gmelinite zone.

The abnormal plumose-calcite aragonite-quartz zone is of the type that might be expected to develop about a locus of hydrothermal activity such as a volcanic centre. Certainly an assemblage very similar in character is encountered in the Tertiary basalts of eastern Iceland about major volcanic centres. However there is a complete absence of independent geological evidence for such a centre in the Antrim Basalts; the intensity of the dyke swarm, usually a sensitive indicator of such centres, is, indeed, lower here than almost anywhere else in Antrim (cf. map in Walker, 1959*b*; Patterson, 1955). The only geological abnormality known to the writer is the presence of an unusually well-developed set of north-west-trending joints in parts of the plumose-calcite zone. It is suggested that the minerals of this zone may have formed under conditions of free circulation of water facilitated by the joints in place of the more stagnant conditions favouring zeolites.

The observation that dolerite or crinanite intrusions (plugs, sills, and dykes) in Antrim bear the same zeolites as the lavas they cut is of considerable significance in connexion with the origin of zeolites in crinanites. It has usually been assumed that the analcime (and presumably the other zeolites that usually occur in crinanites as well) is a primary mineral or is formed during the cooling of the rock. In the Antrim intrusions on

the other hand, it seems clear that, as in the lavas, the zeolites are entirely later than the rock in which they occur. The basalt lavas or the dolerite intrusions merely supply the cavities in which zeolites subsequently crystallize, plus the required chemical raw materials.

Finally, the mapping of the crystal habit of chabazite presents some of the most cogent geological evidence yet found to show that the crystal habit of a mineral, and the twinning, are not due to chance but are controlled by the environment under which the mineral crystallized.

Acknowledgements. My thanks are due to the Keeper of Minerals in the British Museum (Natural History) for permission some years ago to examine the large collection of zeolites, and in particular the collection presented by the late F. N. Ashcroft. Ashcroft's data on five localities no longer accessible (at Ballyhenry and elsewhere) have been made use of in this investigation, and also supplementary data on six other localities. Thanks are also due to Dr. K. C. Dunham and the Geological Survey for permission to examine cores from three boreholes (nos. 2, 8, and 9) at Ballylig, data from these having been incorporated in this study; to Professor W. Q. Kennedy in whose department much of the work was done; to Professor J. K. Charlesworth for encouragement especially in the earlier stages; to Dr. W. Campbell Smith and Dr. J. Watson for critically reading the manuscript; and to Dr. R. J. Davis of the British Museum for confirming identification of gismondine.

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Appendix. The Langford Lodge borehole (Fowler, 1957) passed through some 2 590 ft. of basalts, the greatest thickness known in Antrim. The writer is indebted to the Director of the Geological Survey of Northern Ireland for permission to examine specimens from the bore-

hole, and to publish this note. This part of the borehole was not cored, and the interpretation of the mineral distribution is open to doubt, but a fairly well-defined zonal distribution may be detected.

Chabazite is distributed throughout the borehole and is probably the most abundant zeolite present. In all but the uppermost 300 ft., in which it occurs sporadically, thomsonite is likewise distributed throughout. Levyne is present in most of the samples down to a depth of 1 300 ft., and little is found below that depth. Phillipsite occurs sporadically down to 1 000 ft. Stilbite is first encountered at a depth of 600 ft., and is abundant below 1 000 ft. Mesolite (with scolecite) is sporadically developed below 1 000 ft., but becomes very prominent below 1 700 ft.

In some respects the distribution resembles that found elsewhere in Antrim. However, stilbite is found through a much greater thickness than elsewhere (it is abundant in the lower 1 500 ft. in the borehole), and mesolite, never prominent in surface exposures, is very abundant in the lower 800 ft. in the borehole. Laumontite, extremely rare in surface exposures, is found at several levels below 1 800 ft. These differences may be accounted for by the supposition that the lavas in the Langford Lodge area not only attain an unusually great thickness at present, but originally had a much greater thickness there than elsewhere; the zone containing stilbite, for instance, is consequently 4 or 5 times as thick as it is in the Collin Mtn. area. Indeed, the observed distribution in the borehole bears a much closer resemblance to that in the Tertiary basalts of eastern Iceland, where a much greater thickness of lavas is exposed, and where stilbite and mesolite are both distributed through more than 2 000 ft. of lavas.

It is interesting to note that saponite and calcite are abundant throughout the borehole. This indicates clearly that they cannot be the result of present-day weathering of the lavas.

The Tomhannock Creek, New York, chondrite.

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Summary.—The Tomhannock Creek chondrite has been analysed, with the following results: Fe 11.36, Ni 1.69, Co 0.07, FeS 5.26, SiO₂ 36.88, TiO₂ 0.135, Al₂O₃ 1.80, Cr₂O₃ 0.30, FeO 14.94, MnO 0.31, MgO 23.81, CaO 1.39, Na₂O 0.73, K₂O 0.095, P₂O₅ 0.36, H₂O+ 0.34, C 0.10; total 99.57. The mineralogical composition is olivine (Fo₈₁), hypersthene (En₈₃), plagioclase (An₂₂), nickel-iron, troilite, chromite, and probably apatite. The density of the meteorite is 3.65.

Tomhannock Creek is not identical with Homestead, nor with Yorktown. Yorktown is a chondrite that appears to have fallen near Yorktown, Westchester County, New York (41° 17' N., 73° 49' W.), in September 1869.

THE history of the Tomhannock Creek meteorite is given by Bailey (1887), as follows: 'About the year 1863, Mr. H. Bancker, of Schaghticoke, New York, found, near the base of a large tree on the bank of the Tomhannock Creek in Rensselaer County, a stone of unusual appearance which he took home with him. After breaking off from it a fragment, the stone was laid aside and little further attention given to it until May 1884, when it was sent to the writer who recognized it as an aerolite.'

Curiously enough, the first mention of this meteorite in the literature is not this description by Bailey, but a brief mention by Brezina (1885), under the name 'Ironhannock Creek'. A piece weighing 22 g. was received by Brezina in 1885 (presumably from Bailey) and he describes it as follows: 'Iron hannock Creek dunkel graugrün, ähnlich dem dunkelgrünen Homestead; im Bruch etwas schimmernd, an die Ck erinnernd. Rinde kaum von der Grundmasse zu unterscheiden.' He gave the date of the finding of the meteorite as 1863–64.

In 1895 Brezina was more specific regarding its similarity to Homestead: 'Tom Hannock Creek dürfte vielleicht aus der Reihe der Fallorte

zu streichen sein. Ich habe schon seinerzeit die Aehnlichkeit mit den dunkelgrünen Homestead hervorgehoben; dieselbe ist im Dünnschliffe (den ich seither auch von Tom Hannock machen ließ) ungewöhnlich groß; ebenso stimmt die ganz eigenartige Beschaffenheit der Rinde, welche kaum von der Grundmasse zu unterscheiden ist, bei beiden Steinen völlig überein. Auch in Amerika bezweifelt man die Existenz eines Falles in jener Gegend. Hierher gehört wahrscheinlich auch Yorktown, New York 1869, wovon Siemaschko einen Splitter durch Gregory erhielt; ziemlich dunkles Cg, das den mittleren Partien von Homestead oder den helleren von Tom Hannock entspricht.'

The suggested identity of Tomhannock Creek with Homestead was accepted as proven by LaPaz (1944). He gives no grounds for this statement, and it is presumably based on the work of Brezina.

The original specimen described by Bailey is now in the collection of The American Museum of Natural History (catalogue no. 1034), and can be recognized as such from the drawing and description given by Bailey. On comparing it with specimens of Homestead we cannot agree with Brezina's statements. The two meteorites are quite distinct. A cut surface of Tomhannock Creek is dark chocolate brown; that of Homestead is light grey. These differences are more clearly seen in thin sections; much of the thin section of Tomhannock Creek is almost opaque from finely divided pigment and limonitic alteration products, whereas Homestead is quite unaltered. The composition of the olivine in Tomhannock Creek is Fo_{81} ; that in Homestead Fo_{76} . Thanks to the courtesy of Dr. A. Schiener, of the Naturhistorisches Museum in Vienna, we have been able to examine the specimen and thin section on which Brezina based his description of Tomhannock Creek, and we are at a loss to account for his correlation of this meteorite with Homestead.

The resolution of the confusion between Tomhannock Creek and Homestead does not solve the problem of Yorktown. The identity of Yorktown with Tomhannock Creek has been accepted by later authorities, evidently on the basis of Brezina's statement. The American Museum of Natural History has a specimen labelled Yorktown (catalogue no. 380). This specimen came to the museum with the Bement Collection in 1900, and the accompanying label reads as follows: 'Grey chondrite, Westchester County, New York; fell 1869.' Mr. L. P. Gratacap, who was curator of the collection at that time, commented in the manuscript catalogue: 'Half of a pellet-like mass, grey-white color, chondritic, nickel-iron in flakes and strings; if Tomhannock certainly not the same as the Bement specimen of that fall. . . . This meteorite

referred to Rensselaer County fall, but apparently an Iowa stone. Some mistake.'

Gratacap's statement is correct in so far as the specimen labelled Yorktown is certainly not part of the Tomhannock Creek stone. The only published statement regarding Yorktown seems to be that of Brezina in 1895. Wülfing (1897) records six specimens of Yorktown totalling 216 g. in collections. A search of the files of the U.S. National Museum and of the New York State Museum has failed to yield any information regarding Yorktown. However, Dr. M. H. Hey has kindly examined the files of the British Museum and sent me photostat copies of correspondence between Bailey and J. R. Gregory, and between Bailey and Sir Lazarus Fletcher. This correspondence shows that Bailey obtained the Yorktown material and distributed it. He describes the fall and the finding of the meteorite in a letter to Gregory dated 6 March 1884, as follows: 'The first mentioned (Yorktown) fell in September 1869 (the day I can probably get soon) at Yorktown 7 or 8 miles East of this place [Cortlandt on Hudson, Westchester Co.]. A considerable number of persons in carriages were returning from a Temperance meeting or lecture about 10 p.m. when a brilliant meteor was seen passing from the westward in the same direction (east) and parallel with the road they were travelling, at so low an altitude as to be seen to be between them and a hill or ridge on the other side of a little valley (less than half a mile distant) when it exploded, and the larger portion of the fragment seemed to fall almost directly downward. The detonation was much like a musket shot, but louder, and my informant believes that it burst by striking a large oak tree—of which I have little doubt, from his description of the sound produced by the explosion. The stone I sent was picked up some 10 or 12 years ago, tho the finder cannot locate the exact spot, further than as a little gravelly spot near the foot of a ledge of rock.'

On the basis of Bailey's statement it seems therefore that Yorktown is a genuine fall. Yorktown is a small village in Westchester County, New York, $41^{\circ} 17' \text{ N.}$, $73^{\circ} 49' \text{ W.}$ Of the 216 g. recorded by Wülfing the major part (177 g.) was in Bailey's collection; we do not know the present location of this material.

General description. The appearance of the Tomhannock Creek stone is shown in the photograph (fig. 1). It was originally oblately spheroidal in form, with a diameter approximately 10 cm. The original weight was about 1.5 kg., but pieces have been cut off and distributed, and the present weight of the main mass is 1 082 g. The upper surface of the

stone shown in fig. 1 is marked with prominent 'thumb-prints'. The stone is fine-grained, compact, and hard; a cut surface polishes well, has a dark brown to almost black colour, and shows numerous bright particles of nickel-iron. Contrary to the statement of Brezina, there is



FIG. 1. The Tomhannock Creek meteorite (diameter of stone is 10 cm.).

little if any trace of an original glassy crust: it appears that the stone had lain in the ground and been subjected to weathering for many years before it was found.

The density was determined by placing a weighed piece of the stone in a beaker under a bell jar and evacuating by means of an oil pump. After evacuation carbon tetrachloride was run in, and the apparent loss of weight on suspension in this liquid measured. The density so determined was 3.65.

Mineralogical composition.

The minerals identified in the meteorite are olivine, hypersthene, plagioclase, nickel-iron, troilite, and chromite; a phosphate mineral (apatite or merrillite) is probably present in small amount.

Olivine. The refractive indices are: α 1.674, γ 1.709, indicating a composition of Fo_{81} , according to the determinative curve of Poldervaart (1950). Using the X-ray method of Yoder and Sahama (1957) the composition was found to be Fo_{82} .

Hypersthene. The refractive indices are: α 1.670, γ 1.682, indicating a composition of En_{33} , according to the determinative curve of Kuno (1954).

Plagioclase is present in small amount, and was separated by digesting a sample of the meteorite powder in 1:1 HCl (thereby dissolving nickel-iron, troilite, and olivine), and centrifuging the residue in an acetone-methylene-iodide mixture of density 2.9. The light fraction was a concentrate of plagioclase. Its indices are: α' 1.540, γ' 1.547, indicating a composition of An_{22} .

Nickel-iron. An X-ray powder photograph of nickel-iron separated magnetically from the crushed meteorite shows lines of kamacite and taenite.

A thin section of the meteorite is very dark in colour on account of a great deal of limonitic staining and possibly some fine-grained carbonaceous pigment. It shows numerous chondrules 0.5 to 1 mm. in diameter, of granular olivine or finely prismatic, often radiating hypersthene, set in a finely granular groundmass of olivine, hypersthene, and opaque material. Microscopic examination of a polished surface shows that the grains of nickel-iron are coated with crusts of limonitic material, whereas the sulphide grains appear to be unaffected by weathering.

Chemical composition.

The chemical analysis is given in table I, in the conventional form expressed as oxides, FeS, and metal; in terms of the individual elements; and recalculated on a volatile-free basis. The normative mineral composition, expressed as weight percentages, is also given; this has been calculated as suggested by Wahl (1950), except that we prefer to calculate P_2O_5 as apatite, not merrillite; the composition of merrillite is not well established, being based on a single analysis of a small amount of impure material, and this mineral may well be a variety of apatite.

It should be emphasized that the normative mineral composition

TABLE I. Chemical analysis and normative composition of the Tomhannock Creek meteorite.

A		B		C	D	
Fe	... 11.36	H	... 0.038	—	Nickel-iron	... 13.12 %
Ni	... 1.69	C	... 0.10	—	Troilite	... 5.26 %
Co	... 0.07	O	... 34.612	—	Olivine	... 44.53 %
FeS	... 5.26	Na	... 0.54	0.86	Hypersthene	... 23.88 %
SiO ₂	... 36.88	Mg	... 14.35	22.81	Diopside	... 2.63 %
TiO ₂	... 0.135	Al	... 0.95	1.51	Albite	... 6.18 %
Al ₂ O ₃	... 1.80	Si	... 17.23	27.39	Anorthite	... 1.33 %
Cr ₂ O ₃	... 0.30	P	... 0.16	0.25	Orthoclase	... 0.56 %
FeO	... 14.94	S	... 1.92	—	Apatite	... 0.84 %
MnO	... 0.31	K	... 0.08	0.13	Chromite	... 0.45 %
MgO	... 23.81	Ca	... 0.99	1.57	Ilmenite	... 0.26 %
CaO	... 1.39	Ti	... 0.08	0.13		
Na ₂ O	... 0.73	Cr	... 0.21	0.33		
K ₂ O	... 0.095	Mn	... 0.24	0.38		
P ₂ O ₅	... 0.36	Fe	... 26.31	41.83		
H ₂ O+	... 0.34	Co	... 0.07	0.11		
C	... 0.10	Ni	... 1.69	2.69		
	<u>99.57</u>		<u>99.57</u>	<u>99.99</u>		

A. Chemical analysis expressed as nickel-iron, troilite, and oxides (all H as H₂O, all C as C (both free and combined)).

B. Chemical analysis expressed as elements, with calculated figure for oxygen.

C. Chemical analysis recalculated on a volatile-free (O, C, S, H) basis.

D. Normative composition calculated according to Wahl's method.

calculated from the chemical analysis can only approximate to the actual mineralogy of the meteorite. The calculation involves several arbitrary procedures: Alumina is calculated entirely as feldspar, although it is known that small amounts are present in pyroxene (an analysis of orthorhombic pyroxene from the Miller, Arkansas, chondrite shows 1.22 % Al₂O₃ (Mason and Wiik, 1960)). The TiO₂ is calculated as ilmenite, but the titanium is present wholly or in large part in the ferromagnesian minerals, pyroxene and olivine (the analysis of orthopyroxene from the Miller meteorite shows 0.21 % TiO₂). Nevertheless, when interpreted with care and discrimination, the normative mineral composition provides a useful guide to the actual mineral composition, and conversely the actual mineral composition can be mostly readily correlated with the chemical composition through the calculated norm.

The normative composition correlates well with the observed mineral composition. No diopside was seen, but the small amount of this component is probably in solid solution in the hypersthene. Normative pyroxene is 26.51 %, normative olivine 44.53 %, giving a ratio of pyroxene to olivine of 3:5, which agrees with estimates from thin

sections and X-ray powder photographs. Normative feldspar is 8.07 %, which is probably more than the actual amount of plagioclase, since some of the Al_2O_3 calculated as feldspar will be in the pyroxene. The 0.45 % normative chromite corresponds to the amount seen in polished surfaces. Although neither apatite nor merrillite were observed in thin section, the 0.84 % apatite in the norm could well be present; it would be extremely difficult to recognize in a thin section, since it probably occurs in small grains intimately mixed with pyroxene and olivine.

The proportions of FeO to MgO in the normative pyroxene and olivine are somewhat higher than in the minerals themselves. This is due to the fact that in the analysis all iron not as troilite or as nickel-iron is calculated as FeO, although the stone contains some Fe_2O_3 as limonitic alteration of the metal. Thus some of the oxide iron is present as limonite, not combined in the silicates; the result is that the olivine and pyroxene are poorer in iron than indicated by the norm.

The chemical analysis shows that the Tomhannock Creek stone, in Prior's classification, falls into his group of hypersthene-olivine chondrites of the Baroti and Soko-Banja types. According to the classification of Urey and Craig (1953), it belongs to their H group, since it contains high total iron (26.31 %), the average for the H group being 28.58 %, and for the L group 22.33 %.

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Vaterite from Ballycraigy, Larne, Northern Ireland.

(With Plate XII)

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Summary. Vaterite, the third unstable polymorph of CaCO_3 , is recognized by optical and X-ray powder techniques as a major constituent in a carbonated calcium silicate hydrogel complex formed from larnite at Ballycraigy, Larne, Northern Ireland. Re-indexed X-ray powder data obtained on synthetic vaterite are provided indicating a hexagonal unit cell with dimensions $a = 7.135 \text{ \AA.}$ and $c = 8.524 \text{ \AA.}$, $Z = 6\text{CaCO}_3$. The re-indexing is endorsed by the results of electron diffraction study of synthetic vaterite. Vaterite is shown to correspond to the hypothetical CaCO_3 member of the bastnäsité-synchisite mineral series on the basis of extrapolated cell dimensions and optical properties. A structural scheme for vaterite is proposed in which Ca layers replace the CeF layers in bastnäsité, and near-vertical CO_3 groups are present. The stability relations of natural vaterite are discussed and comment made on the recent observation of vaterite, in a like environment, in carbonated cements and mortars.

THE first accurate description of a third polymorph of CaCO_3 was given by Johnston, Merwin, and Williamson in 1916. It occurred, in certain preparations, as hexagonal plates or lenses yielding a positive uniaxial figure with refractive indices $\epsilon = 1.650$, $\omega = 1.550$, and sp. gr. 2.54. They suggested that the determined density might be low owing to the fibrous nature of the material. An analysis of the purified material was presented (p. 485), and they designated the phase $\mu\text{-CaCO}_3$.

Some little confusion arose subsequently in that other workers, namely Rinne (1924) and Heide (1924), on observing spherulitic aggregates of CaCO_3 identified them, correctly or incorrectly, with similar preparations described by Vater (1893 and subsequent papers). These had already been called vaterite by Meigen (1911). X-ray powder analyses by Rinne (1924) and Heide (1924) showed that the spherulitic aggregates constituted a species of CaCO_3 distinct from calcite or aragonite. The connexion between this spherulitic material and $\mu\text{-CaCO}_3$, as originally defined, was demonstrated by Gibson, Wyckoff, and Merwin in 1925. They showed, by X-ray powder methods, that the two

preparations were identical and distinguished also between spherulitic aggregates of calcite and of $\mu\text{-CaCO}_3$ as prepared by a method due to Bütschli (1908). Spherulites of $\mu\text{-CaCO}_3$ they designated vaterite B, admitting equivalence with the material studied by Rinne and Heide; spherulites of calcite they called vaterite A and suggested that Vater's original preparations comprised principally this material.

Currently all three terms, vaterite, vaterite B, and $\mu\text{-CaCO}_3$ are used in the literature to describe the third polymorph of CaCO_3 . Since X-ray powder data allow of its ready identification regardless of habit the third polymorph of CaCO_3 will be described throughout the present paper simply as vaterite (see also Hey, 1955, p. 76).

Natural occurrence of vaterite. Further examination of hydrogel pseudomorphs after larnite (McConnell, 1954, 1955; Long and McConnell, 1959) showed, in one instance, the presence of a very finely fibrous or platy mineral with high birefringence. In thin section this phase showed some evidence of preferred orientation, in terms of observed birefringence, within the limits of small areas representing pseudomorphed single crystals of larnite. The length of fibres or plates was optically negative and suitable areas, showing uniformly low polarization colours, gave a uniaxial positive interference figure and indicated the possibility of a plate-like habit for the mineral.

The highly birefringent material was observed only in very minor amount in one thin section and from this a small fragment was removed for optical, microchemical, and X-ray examination. The refractive index of the material was determined as 1.491 and part of the fragment, when placed in dilute HCl, dissolved with vigorous effervescence leaving a silica-gel pseudomorph. An X-ray photograph taken on a single crystal camera using oscillation technique showed no evidence of preferred orientation effects and its character suggested that the size of the individual crystals present was very small indeed since a normal powder photograph was obtained from the small fragment used (volume 0.001 mm.^3). The absence of appreciable line broadening on the photograph defined a lower size limit of 0.1μ approximately. The powder photograph yielded the d spacings listed in table I, and comparison with available data indicated that the material is vaterite (A.S.T.M. 1-1033, 4-0844).

At this stage it was realized that the material studied was composite, comprising vaterite in extremely intimate association with a hydrogel phase in the pseudomorphs studied. This conclusion accords with the low refractive index of the composite material (1.491 as compared with

TABLE I. X-ray powder data for natural vaterite from Ballyeraigy.
Cu- $K\alpha$ radiation.

d , Å.	I .	d , Å.	I .
4.25	vw	1.853	w
3.57	s	1.820	m
3.28	s	1.647	w
2.728	s	1.309	vvw
2.062	ms	1.286	vw

refractive indices for vaterite, $\omega = 1.550$, $\epsilon = 1.650$), the presence of a silica gel residue on treatment with dilute HCl, and the absence of any indication of a second phase in the X-ray powder analysis (the hydrogels studied previously yielded X-ray diffraction maxima only on lengthy exposure).

Synthesis of vaterite. Vaterite was subsequently synthesized in quantity to obtain more accurate and complete X-ray powder data for comparison. Initially the method recommended by Gibson and others (1925) was used but was only partly successful; vaterite in the form of hexagonal plates and lenses was observed but not in sufficient amount and purity, the main components being aragonite with minor amounts of calcite. Vaterite was prepared in bulk, and free from both calcite and aragonite, as follows: A 0.1 M solution of calcium chloride was added, very slowly and with careful stirring, to a solution of 50 g. of K_2CO_3 in 700 ml. of water, containing 300 p.p.m. of Calgon,¹ maintained at 60°C. Vaterite began to crystallize only when the solution was appreciably supersaturated with respect to calcite and aragonite, and crystallized in the form of minute spherulitic crystal aggregates of the order of 10 μ in diameter.

These spherulites were optically positive. Synthetic aragonite from the earlier experiments and synthetic vaterite with spherulitic habit are illustrated in plate XII.

X-ray powder data. An X-ray diffractometer trace of synthetic vaterite showed appreciable line broadening effects, which were equated with small crystal size. Data obtained from a standard X-ray powder photograph are listed in table II.

A hexagonal unit cell with dimensions $a = 7.135$ Å., $c = 8.524$ Å., and $Z = 6CaCO_3$, calculated density 2.65, was indicated. Intensity maxima with $h-k = 3n$ were very much stronger than those with $h-k \neq 3n$ indicating a pseudocell with $a' = a\sqrt{3}$ and $c' = c$. The

¹ Commercial sodium hexametaphosphate.

pseudocell, with $Z = 2\text{CaCO}_3$, corresponds to the unit cell defined by Olshausen (in Heide, 1924, and Olshausen 1924).¹

TABLE II. Indexed X-ray powder data for synthetic vaterite. Camera diameter 9.0 cm., radiation Cu- $K\alpha$. Intensities from visual comparison.

<i>I.</i>	<i>d</i> , Å.	$\sin^2\theta$		<i>I.</i>	<i>d</i> , Å.	$\sin^2\theta$		<i>I.</i>	<i>d</i> , Å.	$\sin^2\theta$	
		obs.	calc.			obs.	calc.			obs.	calc.
m	4.26	0.0327	0002	0.0327	vw	1.185	0.4230	505̄2	0.4218		
s	3.58	0.0463	112̄0	0.0467	w	1.166	0.4370	246̄0	0.4358		
s	3.30	0.0545	112̄1	0.0549	w	1.141	0.4565	145̄4	0.4577		
s	2.73	0.0796	112̄2	0.0794	w	1.112	0.4808	224̄6	0.4812		
wb	2.33	0.1098	123̄0	0.1090	w	1.064	0.5254	0008	0.5235		
	2.30	0.1124			w	1.034	0.5557	156̄3	0.5561		
w	2.23	0.1200	112̄3	0.1203	w	1.019	0.5727	112̄8	0.5702		
w	2.127	0.1314	0004	0.1309	w	0.979	0.6205	145̄6	0.6213		
s	2.059	0.1401	303̄0	0.1401	w	0.964	0.6395	257̄2	0.6397		
w	1.856	0.1725	303̄2	0.1728	w	0.946	0.6648	303̄8	0.6636		
s	1.825	0.1784	112̄4	0.1776	w	0.913	0.7132	336̄6	0.7147		
wb	1.648	0.2189	224̄2	0.2195	w	0.877	0.7726	404̄8	0.7725		
vw	1.544	0.2492	404̄0	0.2490	w	0.872	0.7823	347̄5	0.7804		
vw	1.480	0.2715	303̄4	0.2710	w	0.862	0.7989	707̄2	0.7953		
vw	1.416	0.2965	235̄0	0.2957	w	0.836	0.8494	145̄8	0.8504		
vw	1.369	0.3171	224̄4	0.3176	w	0.826	0.8701	347̄6	0.8703		
w	1.316	0.3429	112̄6	0.3412	w	0.814	0.8961	178̄1	0.8953		
vw	1.288	0.3585	145̄2	0.3596							

Choice of the larger unit cell justifies arguments by Bunn (1945, p. 285), who pointed out that the CO_3 groups in vaterite must be vertical to account for the observed optical sign, but this being the case, vaterite could not at the same time be hexagonal (or trigonal) with $Z = 2\text{CaCO}_3$.

Electron diffraction data. Synthetic vaterite from the bulk sample was used for electron optic and diffraction studies using a Siemens Elmiskop 1 operating at $100 \text{ kV} \pm 3\%$. The smallest crystal fragments studied (0.2μ) were composite and yielded only preferred orientation diffraction patterns one of which is illustrated in fig. 1. This diffraction pattern

¹ Olshausen's later data (1924, p. 485) on conversion from kX agree closely with the present results: $\sqrt{3} a' = 7.133 \text{ Å}$, $c = 8.540 \text{ Å}$. They appear to be more accurate than his earlier values as quoted by Heide (1924, p. 650), which are currently quoted in the literature and which on conversion give: $\sqrt{3} a' = 7.150 \text{ Å}$, $c = 8.573 \text{ Å}$. (cf. Wyckoff, 1931). A note to the effect that the true unit cell for vaterite has $a = \sqrt{3} a'$ appears, in the form of a personal communication from Wickman (1952), in Graf and Lamar, 1955. There is no evidence to suggest that this conclusion was reached by re-indexing X-ray powder data.

was indexed but no attempt was made to derive accurate d spacings and cell parameters from it.¹

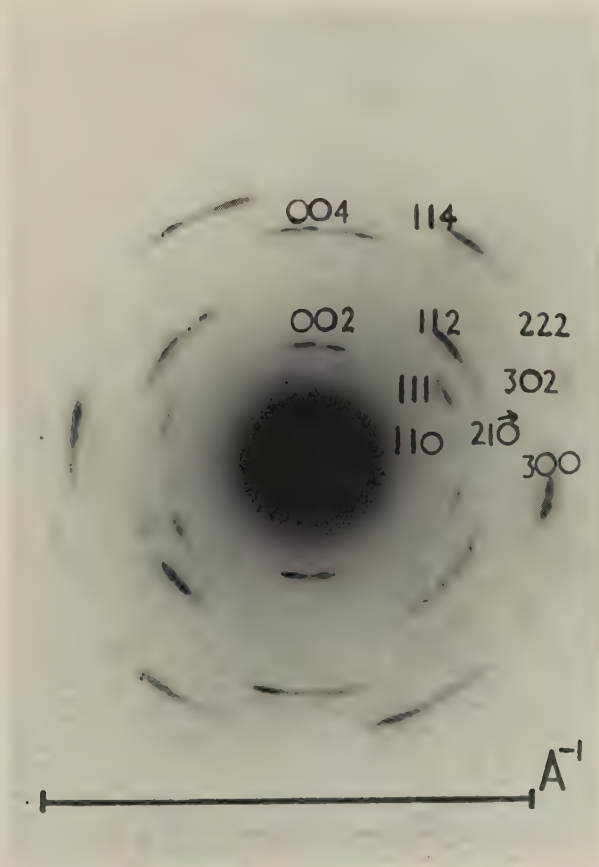


FIG. 1. Preferred orientation electron diffraction photograph of synthetic vaterite.

Uncorrected d spacings and the indices of the diffraction maxima are set out in table III. On the preferred orientation electron diffraction photograph it was possible to demonstrate the presence, in the correct

¹ The d spacings given are correct to $\pm 3\%$, a limit set by the on-off high-voltage fluctuation on the electron microscope. It was inconvenient to use an internal standard in the present diffraction experiments. (In order to match the data given in table III with the X-ray diffraction data the former require to be scaled linearly by a factor of approximately 1.013.)

position, of weak intensity maxima $21\bar{3}0$ and $40\bar{4}0$, for which $h-k \neq 3n$, indicative of the larger unit cell chosen on the basis of X-ray powder indexing.

TABLE III. Electron diffraction data for synthetic vaterite.

d , Å.	I .	hkl .	d , Å.	I .	hkl .
4.18	s	0002	1.83	w	$30\bar{3}2$
3.58	m	$11\bar{2}0$	1.80	s	$11\bar{2}4$
3.27	m	$11\bar{2}1$	1.62	w	$22\bar{4}2$
2.69	s	$11\bar{2}2$	1.53	vw	$40\bar{4}0^*$
2.28	vw	$12\bar{3}0^*$	1.28	w	$14\bar{5}2$
2.10	s	0004	1.05	w	0008
2.03	s	$30\bar{3}0$			

* $h-k \neq 3n$.

The relationship of vaterite to the mineral series bastnäsite-synchisite.

In 1953 Donnay and Donnay presented an account of the bastnäsite-synchisite mineral series, demonstrating definite stoichiometric ratios of CeFCO_3 and CaCO_3 for the minerals parisite, röntgenite, and synchisite in terms of measured cell parameters, structure, and optical properties. The relevant data are summarized in fig. 2 of this paper.

In the course of the present work it became obvious that vaterite must be equated with the CaCO_3 end-member of the bastnäsite-synchisite series. Fig. 2, which illustrates the linear gradation in cell parameters and optical properties in this series, has been drawn to demonstrate this relationship. The full lines are due to Donnay and Donnay, the dotted extrapolations are due to the present author.

Donnay and Donnay (op. cit.) discussed the structural aspects of the bastnäsite-synchisite series in terms of the structure of bastnäsite, space group $P\bar{6}2c$, indicating that the CeF layers of the bastnäsite structure are replaced regularly, and in definite sequence and proportion, by Ca layers in the compounds parisite, röntgenite, and synchisite. It is natural to extend their structural argument to vaterite, which since it is optically positive must, *a priori*, have vertical CO_3 groups. To a first approximation the structure of vaterite may be derived by replacing all the CeF layers of bastnäsite with Ca layers. The space group $P\bar{6}2c$ is no longer admissible, however, since a strong $11\bar{2}1$ intensity maximum has been recorded both from X-ray and from electron diffraction experiments (for $P\bar{6}2c$, $hh\bar{2}hl$ should appear with l even only). Further, the unit cell of vaterite shows considerable collapse in the c direction ($c = 8.524$ Å.) relative to that of bastnäsite ($c = 9.787$ Å.), ruling out the

possibility of a vertical stacking sequence of CO_3 groups identical with that of bastnäsite.

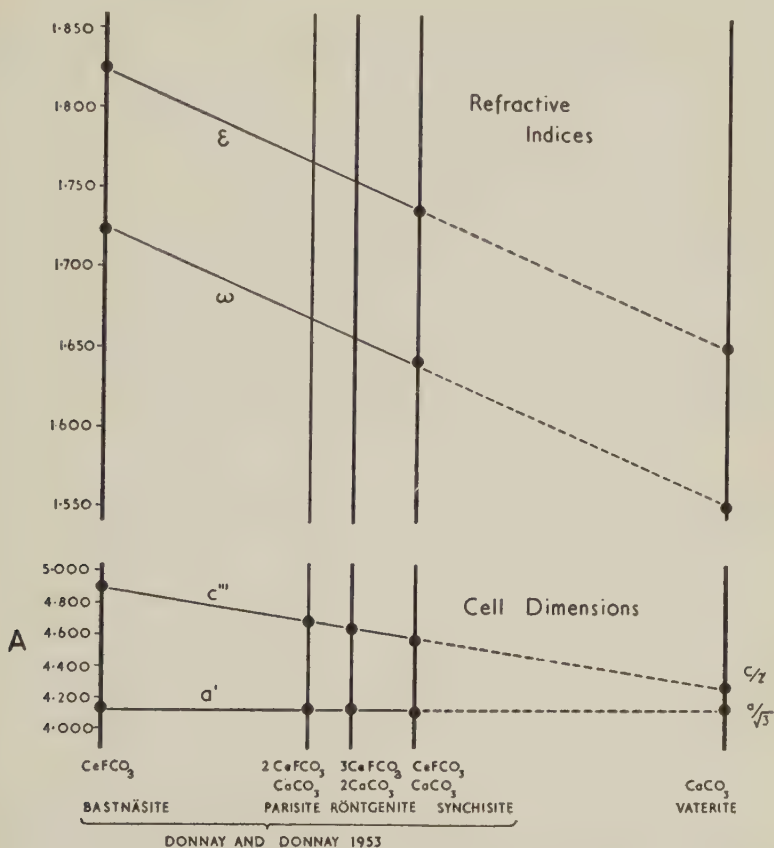


FIG. 2. Cell dimensions and refractive indices in the mineral series bastnäsite-vaterite. Data on the series bastnäsite-synchisite from Donnay and Donnay, 1953.

In this connexion Donnay and Donnay (op. cit., p. 950) considered that the CO_3 groups in a structural unit between adjacent CeF and Ca layers in parisite, röntgenite, and synchisite require to be tilted out of the vertical plane since the distance between such layers is only $4.56 \text{ \AA}$. as compared with $4.89 \text{ \AA}$. in the bastnäsite structure. This collapse of $0.33 \text{ \AA}$. is close to half the corresponding collapse between adjacent Ca layers in the vaterite structure, which equals $0.63 \text{ \AA}$. It is impracticable

to consider, in the latter case, that the collapse is due solely to tilting of the normal to the CO_3 group out of the horizontal plane since this degree of tilt ($\approx 29^\circ$) can readily be shown to produce material reduction in the optical birefringence. Comparison of the observed birefringence of vaterite (0.100–0.102, Gibson *et al.*, 1925, pp. 327 and 331) and bastnäsite (0.101, average of eight values quoted by Donnay and Donnay, *op. cit.*, p. 960, table 7) suggests rather that the CO_3 groups remain vertical in vaterite but require to be offset in vertical sequence. This is possible because the sites occupied by F ions in the bastnäsite structure are unoccupied in vaterite.

Further work on the structure of vaterite must await more complete diffraction data, which may possibly be obtained by electron-diffraction technique on better crystallized material.

Stability relationships of vaterite. Vaterite is unstable in the presence of water at room temperature and pressure, dissolving readily with concomitant precipitation of calcite; on heating, in the dry, at 400°C . it transforms to calcite in a few minutes (Johnson *et al.*, 1916; Lucas, 1947).

The occurrence of vaterite in the natural environment accordingly requires explanation since it must be considered to have some considerable measure of stability in this instance.

Two primary factors that may control the formation and preservation of a metastable phase may be considered here. The initial precipitation of a metastable phase may be induced by conditions of supersaturation in solution; this in practice constitutes the basis of the methods by which vaterite has been synthesized. The other important factor is the influence of structures already present in the case of a reaction that proceeds essentially within a solid medium; in this case a considerable measure of stability may be derived for the metastable reaction product owing to co-operative effects. In such cases it is clearly no longer possible to consider the stability relationships of the metastable phase independently of its environment, in particular if it is finely crystalline and intimately associated with an additional phase.

It is primarily on the basis of the second of the above factors that one may usefully seek to explain the development of vaterite in a hydrogel complex at Ballycraigy. There can be little doubt that its initial development was due to the carbonation of a high-lime hydrogel (Long and McConnell, 1959) and that in this case the presence of imperfectly crystalline $\text{Ca}(\text{OH})_2$ would favour the development of the layer type vaterite structure. Comparison of the cell-dimensions of vaterite and

portlandite also favours this conclusion. The ready breakdown of vaterite to calcite was observed in thin section.

An analogue to the natural carbonation process, in which vaterite is developed, has recently been described by Cole and Kroone (1959). These authors point out that vaterite occurs at an early stage in the carbonation of cements and mortars, and they suggest a sequence of hydration-carbonation reactions for cement minerals that constitutes a close parallel to the natural hydration-carbonation reaction sequence as observed for larnite and bredigite at Ballycraigy. They cite the following steps: anhydrous cement minerals $\longrightarrow$ siliceous residue + calcium hydroxide $\longrightarrow$ ill-crystallized vaterite, calcite, and aragonite $\longrightarrow$ well-crystallized calcite. The corresponding steps in the natural hydration-carbonation process are: β - Ca_2SiO_4 , by solid-state hydration at high pH under CO_2 -deficient conditions $\longrightarrow$ a high-lime hydrogel, $1.5 \text{ CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ (Long and McConnell, 1959), then by carbonation $\longrightarrow$ a vaterite-hydrogel complex, which breaks down $\longrightarrow$ calcite + a siliceous residue.

Recognition of vaterite as the end member of the bastnäsite-synchisite mineral series suggests that more careful study will show that vaterite occurs, possibly in syntectic intergrowth with synchisite, in carbonatite paragenetic environments. Some evidence of this is already provided in that paramorphs of calcite after vaterite have been described recently by Ilyinsky (1958).

To the best of the author's knowledge vaterite has not previously been recorded as a natural mineral. It is known to occur in the repair tissue of certain young gastropods (Mayer and Weineck, 1932), in urinary calculi (Prien and Frondel, 1947), and, as already noted, as a carbonation product in hydrated cements and mortars (Cole and Kroone, 1959).

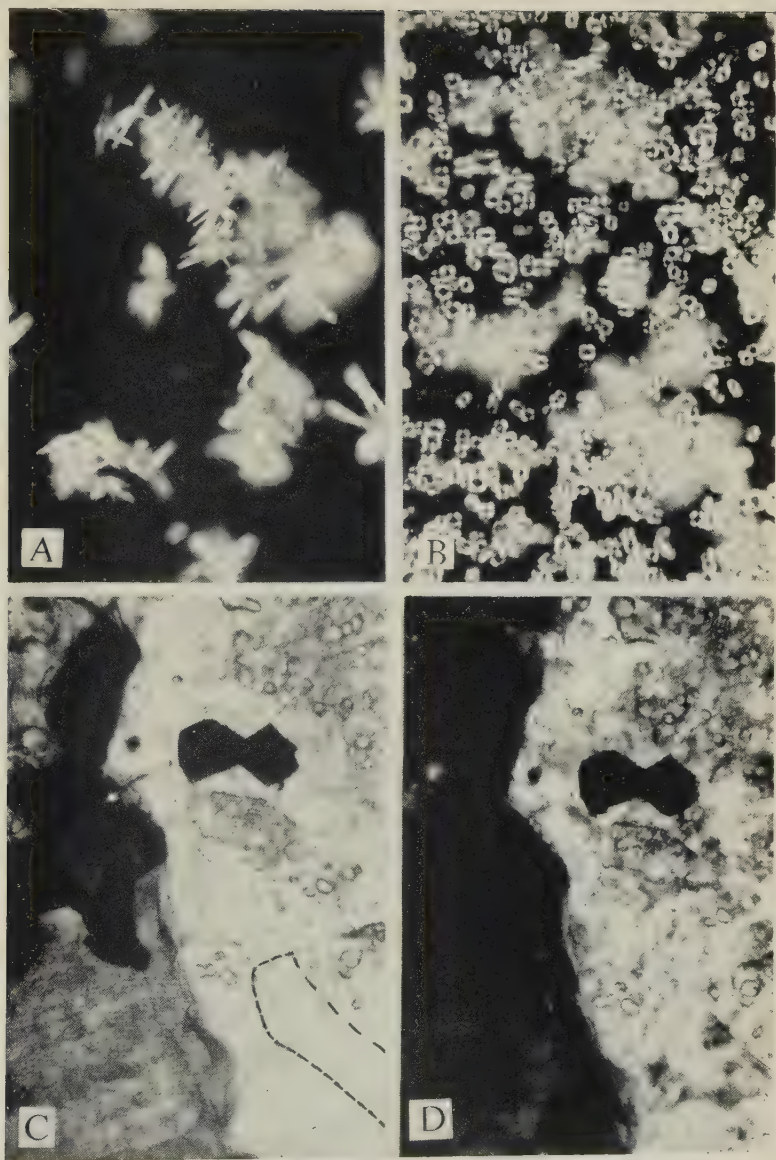
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EXPLANATION OF PLATE XII.

- FIG. A. Synthetic aragonite; crossed nicols, $\times 220$.
- FIG. B. Synthetic vaterite; crossed nicols, $\times 220$.
- FIG. C. Vaterite in hydrogel pseudomorphs after larnite. The limits of one pseudomorphed grain have been indicated; ordinary light, $\times 220$.
- FIG. D. As in C but with crossed nicols, $\times 220$.
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J. D. C. McCONNELL: VATERITE FROM BALLYCRAIGY, LARNE,
NORTHERN IRELAND

β -Ferric Oxyhydroxide.

By A. L. MACKAY, M.A., Ph.D., F.Inst.P.

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[Taken as read 31 March 1960.]

Summary. The crystallographic properties of the hydrated iron oxide obtained by the hydrolysis of FeCl_3 are described. The characterizing X-ray powder pattern can be indexed on a tetragonal unit cell with a 10.48 and c 3.023 Å. This cell is shown to contain eight formula units of FeOOH but Cl⁻ or other anions are necessary for the crystallization of the material. The structure is that of hollandite or $\alpha\text{-MnO}_2$. The unit cell has been confirmed by electron diffraction from single crystals having dimensions about $5000 \times 500 \times 500$ Å. and twinning, which produces hexagonal stars, has been studied. On heating, the structure breaks down and recrystallizes as $\alpha\text{-Fe}_2\text{O}_3$, probably with an intermediate stage involving a spinel phase.

β -FERRIC oxyhydroxide is one of the less common iron oxides and its study has been somewhat neglected as large crystals have not so far been reported. Its crystal chemistry appears to be markedly different from that of the other iron oxides and deserves a more detailed study than hitherto. Evidence for the formula is presented below, but for brevity it will be used at once. The material under discussion is characterized by the X-ray powder measurements quoted in table I.

TABLE I. X-ray powder data for $\beta\text{-FeOOH}$.

<i>hkl.</i>	<i>d.</i>	<i>I.</i>	<i>hkl.</i>	<i>d.</i>	<i>I.</i>
110	7.40 Å.	vs	501	1.719	vw
200	5.25	m	431		
220	3.70	vw	521	1.635	vs
310	3.311	vs	002	1.515	m
400	2.616	m	611	1.497	w
211	2.543	s	112	1.480	w
420	2.343	w	710		
301	2.285	m	550		
321	2.097	w	640	1.459	vw
510	2.064	w	541	1.438	s
411	1.944	ms	730	1.374	m
440	1.854	vw	312		
600	1.746	m	Indexing then becomes uncertain.		

Occurrence. $\beta\text{-FeOOH}$ is produced in the following processes of which the first is the most important:

The hydrolysis of FeCl_3 or FeF_3 in solution at 60–100° C. for about

6 hours. If the hydrolysis is very protracted (144 hours) α -Fe₂O₃ results, not α -FeOOH as in the case of all other iron salts examined (except ferrous ammonium sulphate), so that β -FeOOH is presumably metastable at this temperature.

Direct precipitation from 0.5 M FeCl₃ at 75° C. by the addition of 3.5 M K₂CO₃ has been reported (Hofer *et al.*, 1946).

The damp oxidation of crystals of FeCl₂·4H₂O. Crystals of this material accessible to the atmosphere for a year had formed a brown powder identified as β -FeOOH.

The dry oxidation of 3Fe(OH)₂·FeCl₂ (Keller, 1948, see below).

The damp oxidation of 'white rust' formed on steel under reducing conditions in contact with sea water (Aruja, private communication, 1958).

The hydrolysis of FeOCl (Heller, Kratky, and Nowotny, 1936).

Various natural processes give an iron-containing scum that may be β -FeOOH (Kratky and Nowotny, 1938).

X-ray powder photographs. The spacings listed in table I agree well with those published earlier—ASTM cards numbers 1-0669, 3-0429, and 3-0446; Weiser and Milligan (1935); Kratky and Nowotny (1938); Mackenzie (1952). Weiser and Milligan indexed their data, which did not include the first line at 7.40 Å., on an orthorhombic cell with *a* 5.28, *b* 10.24, and *c* 3.34 Å. Kratky and Nowotny revised this to *a* 10.56, *b* 10.24, and *c* 3.03 Å., having better data from a texture photograph (that is, a powder photograph showing preferred orientation effects), but the spacings can, in fact, be indexed on a body-centred tetragonal cell with *a* 10.48 ± 0.01 and *c* 3.023 ± 0.005 Å. There is no evidence of the doublets such as 200, 020 which might be expected if the material were orthorhombic. The powder lines continue sharp up to the $\lambda/2$ cut off (0.895 Å.).

Composition. The principal chemical study of β -FeOOH is by Weiser and Milligan (1935) who established the formula and showed that the compound always contains chlorine. When first precipitated the chlorine content might be as high as 8 % (Fe/Cl = 4.79), but with prolonged washing this can be reduced to any desired value (certainly to Fe/Cl > 45). Analyses kindly made for us at the Building Research Station showed 2 to 4 % chlorine and no ferrous iron. The water content is somewhat uncertain as much of the water is certainly adsorbed. Dehydration curves recorded on a thermo-balance with a rate of heating of 100° C. per hour and an uncontrolled water vapour pressure over the specimen showed a loss of some 10 % water below 100° and a further 13.5 % in a

sharp step at about 230° C. A loss of 10 % would be expected from the stoichiometric composition. Weiser and Milligan found that the step occurred over a broader temperature interval as the Cl content was

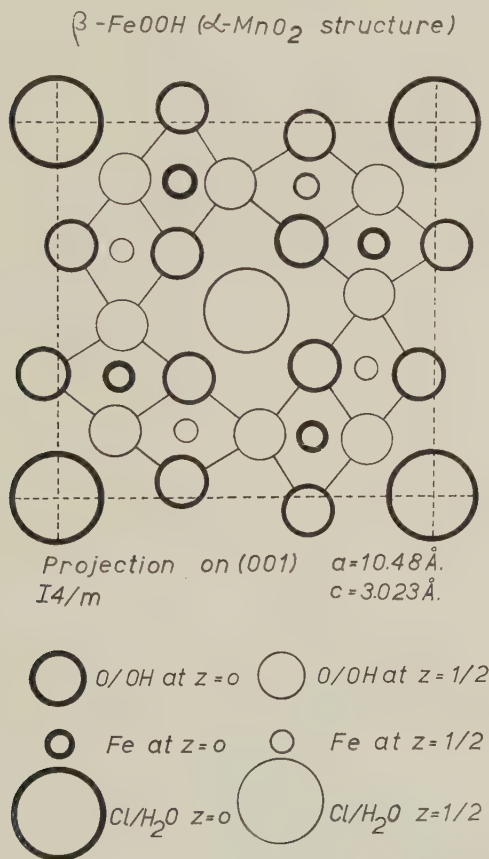


FIG. 1. Projection of the α -MnO₂ structure as determined by Byström and Byström (1950).

lowered. The product of the dehydration is α -Fe₂O₃. The observed density is 3.0 g./cm.³, whereas if the unit-cell contents were 8FeOOH the calculated density would be 3.6 g./cm.³ The large discrepancy can probably be ascribed to adsorbed water, since the crystals are very small.

Structure. On the basis of the unit-cell dimensions and the observed body-centring of the cell it was suggested (Bernal, Dasgupta, and

Mackay, 1959) that β -FeOOH has essentially the hollandite ($\text{BaMn}_8\text{O}_{16}$) or α - MnO_2 structure (fig. 1). This has now been confirmed by the comparison of observed and calculated intensities (fig. 2). The intensities

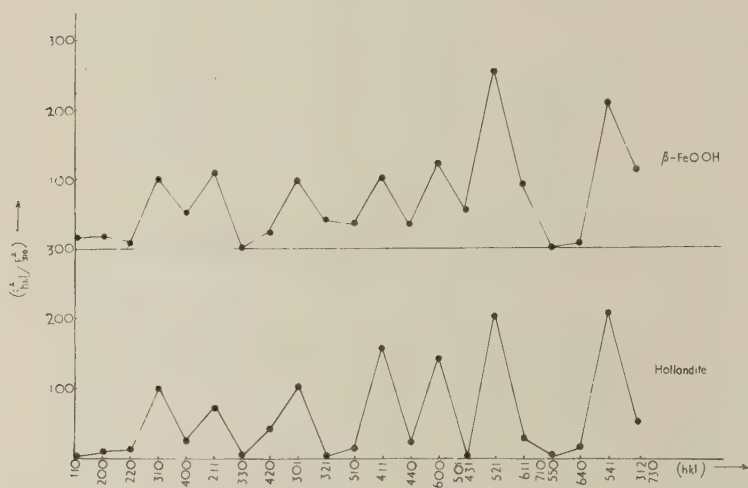


FIG. 2. Comparison of the intensities observed for β -FeOOH (powder photograph) with those calculated for hollandite by Byström and Byström (1950).

were calculated by Byström and Byström (1950), who determined the structure of hollandite, for Mn^{4+} ions (21 electrons) but the agreement did not improve appreciably on recalculating them for Fe^{+++} ions (22 electrons). In view of the uncertainty as to the contents of the channels in the structure (see below) the agreement is satisfactory. The structure analysis could not easily be continued because of the overlapping of the $hk0$ and $k\bar{h}0$ reflections in the powder photographs and the impossibility of distinguishing between the Laue groups $4/m$ and $4/mmm$.

Agreement with Byström and Byström's observations implies a space group $I4/m$ with 8Fe in $8(h)$ positions with parameters (0.348, 0.167, 0) and 16 (O, OH) in $8(h)$ positions with parameters (0.153, 0.180, 0) and (0.542, 0.167, 0). There may be Cl' ions or H_2O molecules in the $2(b)$ positions.

Crystal chemistry. The Fe^{+++} ions are each surrounded octahedrally by six (O'' , OH') ions. These octahedra are linked to form double strings parallel to the c -axis. In each string the octahedra share edges parallel

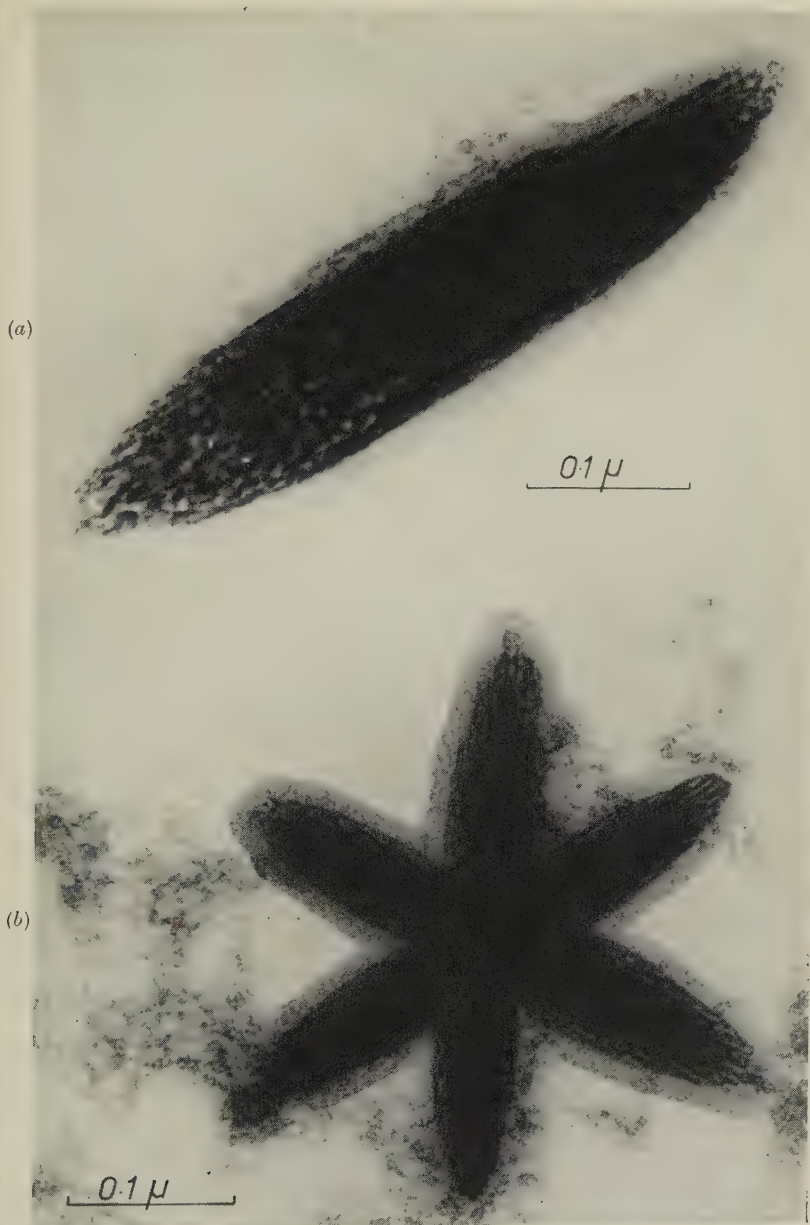


FIG. 3. (a) Single crystal of β -FeOOH. (b) Star-shaped twinned crystal of β -FeOOH.

to a and each octahedron shares also two edges with octahedra in the neighbouring string. The double strings are joined by sharing corners. The $2(b)$ positions at $(0, 0, 1/2)$ are surrounded by 8 ± 4 (O'' , OH') ions. If the $2(b)$ positions were filled by oxygen atoms the structure would

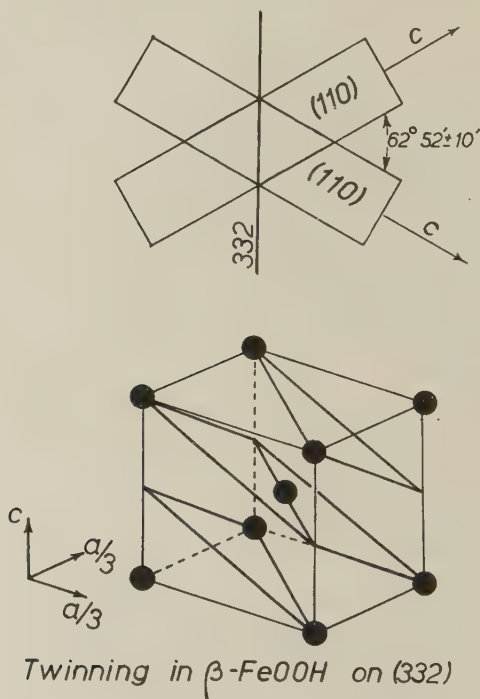


FIG. 4. The twin law for β -FeOOH.

consist of approximately body-centred close-packed oxygen. The parameters would be $(0.167, 0.167, 0)$ and $(0.500, 0.167, 0)$ instead of those quoted above. In hollandite the $2(b)$ positions are occupied statistically to the extent of 50 % by Ba^{++} ions. In β -FeOOH these positions will be available for the large Cl' ions but the diameter of such an ion ($3.62 \text{ \AA}$) is greater than the c -dimension of the cell ($3.02 \text{ \AA}$) so that they could only be accommodated statistically. The maximum chlorine content ($Fe/Cl = 4.79$; Weiser and Milligan, 1935) would correspond to about 84 % occupation of the $2(b)$ positions, and, if all the $2(b)$ positions were occupied by H_2O molecules after washing, the formula would correspond to $Fe_2O_3 \cdot 3/2 H_2O$, more in accord with the dehydration data.

Hollandite is reported to have ion exchange properties. The F'-containing β -FeOOH had exactly the same cell dimensions as the Cl'-containing samples and no changes dependent on Cl' content were found. Presumably some OH' ions replace O'' ions to compensate for the extra

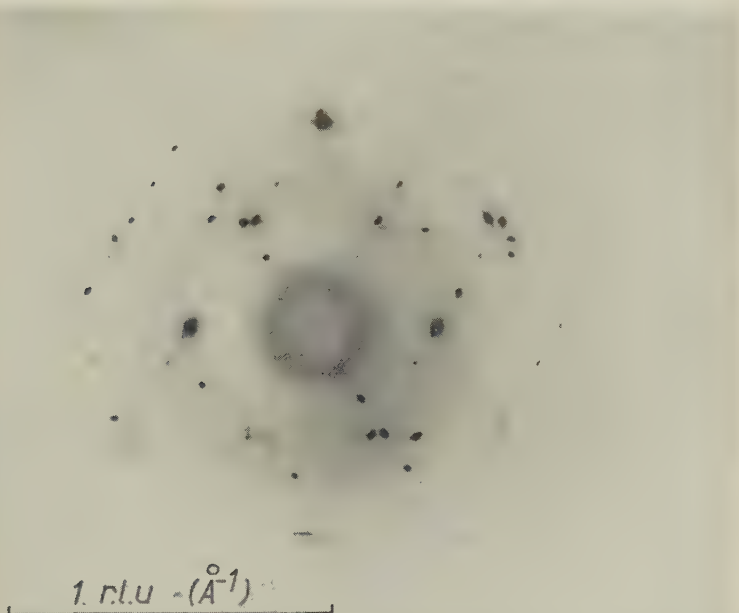


FIG. 5. Electron diffraction pattern from an X-shaped twin of β -FeOOH lying in the orientation shown in fig. 4.

negative charge of the Cl'. It is interesting to compare the 'ferroxdure' compounds ($\text{BaFe}_2^{++}\text{Fe}_{16}^{+++}\text{O}_{27}$ and $\text{Ba}_2\text{Fe}_2^{++}\text{Fe}_{28}^{+++}\text{O}_{46}$; Braun, 1957), where Ba replaces O in a close-packed arrangement, with hollandite.

Electron microscopic and diffraction observations. Specimens of β -FeOOH were examined by electron microscopy and were seen to be composed of exceptionally regularly formed spindle-shaped crystals of length about 5 000 Å. (fig. 3a). This agrees with Meldau's observations (1957). Many star-shaped and X-shaped twins are found (fig. 3b). The crystals obtained by the hydrolysis of FeF_3 occurred in irregular aggregates but nevertheless gave the powder diffraction pattern of β -FeOOH. Single crystal diffraction patterns were obtained from crystals such as that of fig. 3a showing that the elongation is along the

c-axis and confirming the cell dimensions. Unfortunately all crystals examined lay with their *c*-axes parallel to the substrate so that it was not possible to check differences in intensities between *hkl* and *khl* reflections. Crystals were found with (100), (110), or (310) parallel to the substrate. The components of the twinned crystals, however, lay only on (110) and the twin plane was shown to be (332) (figs. 4 and 5). It has been shown that the structure is built up of oxygen atoms close-packed in a body-centred cubic lattice, and if referred to the pseudo unit-cell (cubic with cell edge $a/3 = c$) the twin plane has indices (112), which are the indices of the usual twin plane in α -iron and α -tungsten.

Formation of β -FeOOH from $\text{Fe}_2(\text{OH})_3\text{Cl}$. Keller (1948) reported the formation of a compound $\text{Fe}_2(\text{OH})_3\text{Cl}$, which was isomorphous with one of the four forms of $\text{Cu}_2(\text{OH})_3\text{Cl}$, probably with atacamite, the orthorhombic form determined by Thoreau and Verhulst (1938), when a solution of FeCl_2 was incompletely precipitated with NaOH . When this compound is oxidized dry then β -FeOOH is formed. Fig. 6 shows an oriented texture of needles, which fig. 7 proves to be β -FeOOH, resulting from the decomposition of a flaky crystal, presumably $\text{Fe}_2(\text{OH})_3\text{Cl}$.

Transformation of β -FeOOH on heating. When β -FeOOH is heated in air α - Fe_2O_3 eventually results, but there are several indications that there may be intermediate stages to the process. Firstly, we have observed that sometimes, if the heating is stopped at an intermediate temperature, a magnetic product may result. One explanation was that a disordered form of α - Fe_2O_3 , perhaps superparamagnetic like δ -FeOOH, intervened. Further heating in this case would destroy the ferromagnetism by producing recrystallization as normal α - Fe_2O_3 . Hilpert, Maier, and Hoffman (1938) also observed ferromagnetism on hydrolysing and then dehydrating FeOCl . By itself β -FeOOH has the abnormally low bulk susceptibility for an iron oxide of $29.0 \pm 0.5 \times 10^{-6}$ e.m.u. (Hofer *et al.*, 1946). Secondly, Mackenzie (1952) found that the d.t.a. record of the dehydration of β -FeOOH showed an endothermic peak at 250–260° C. corresponding to the loss of water but also an exothermic peak at a higher temperature (420° C.) which was first attributed to recrystallization of the α - Fe_2O_3 but which must now be given another explanation (see below). Thirdly, the state of β -FeOOH immediately on dehydration is certainly peculiar because Fischer-Tropsch catalysts, prepared by the reduction of precipitated oxide in H_2 at 300° C., have no activity if β -FeOOH is the initial material. Other oxides, even if chlorides are present, give catalysts active in promoting the

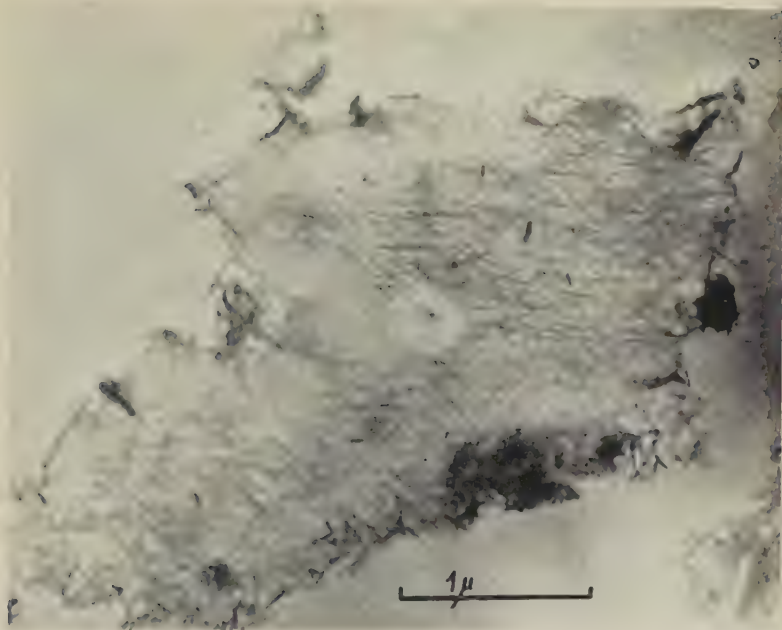


FIG. 6. An oriented texture of needles of β -FeOOH probably deriving from the breakdown of a crystal of $\text{Fe}_2(\text{OH})_3\text{Cl}$.

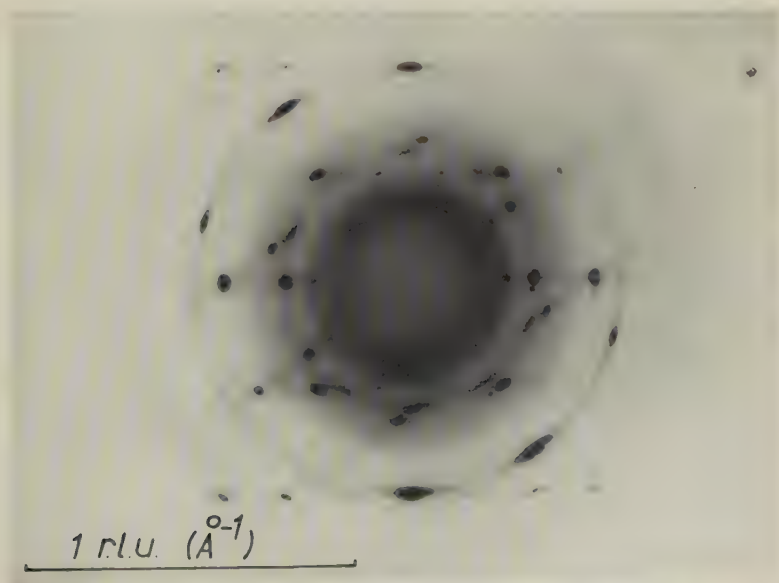


FIG. 7. Electron diffraction pattern from the texture of needles shown in fig. 6.

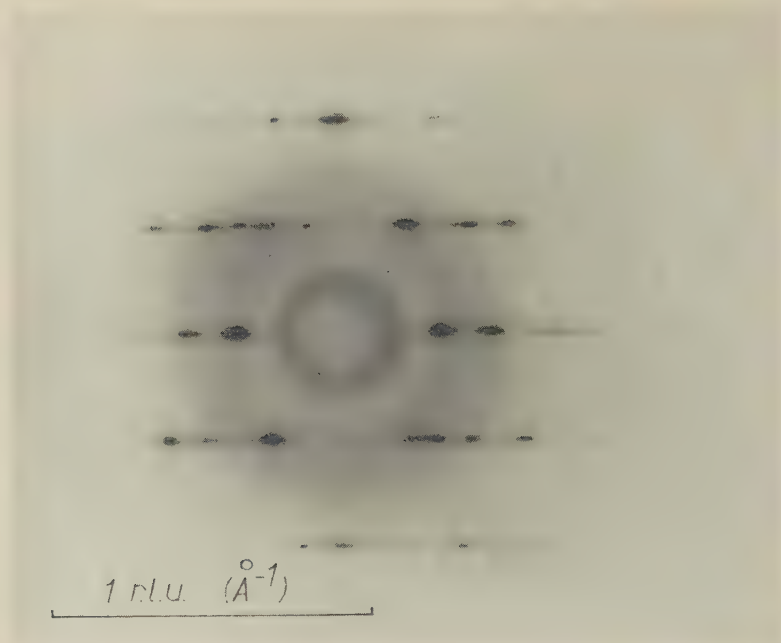


FIG. 8. Electron diffraction pattern from a single crystal of β -FeOOH after heating showing streaks perpendicular to [001].

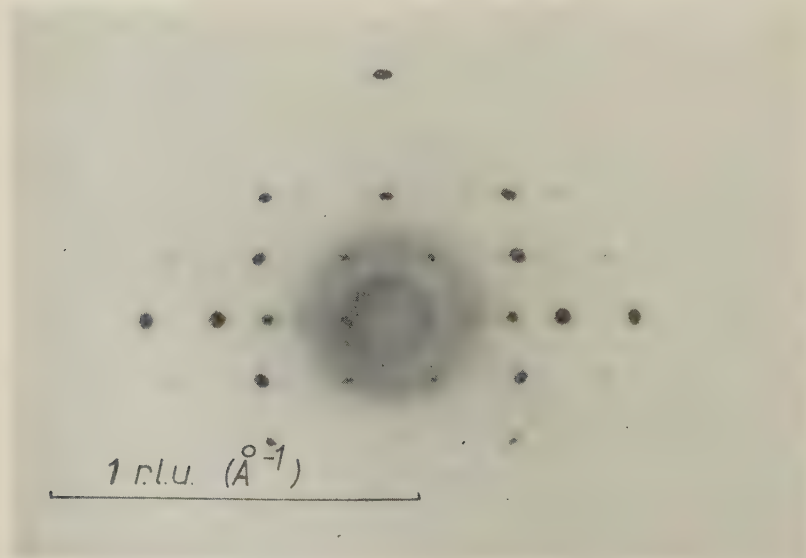


FIG. 9. Electron diffraction pattern from a single crystal of β -FeOOH that has completely transformed to crystals with a spinel structure in two orientations.

combination of CO and H_2 . Even if the β -FeOOH is first aged to α -Fe₂O₃ before reduction no catalytic activity is found (Hofer *et al.*, 1946).

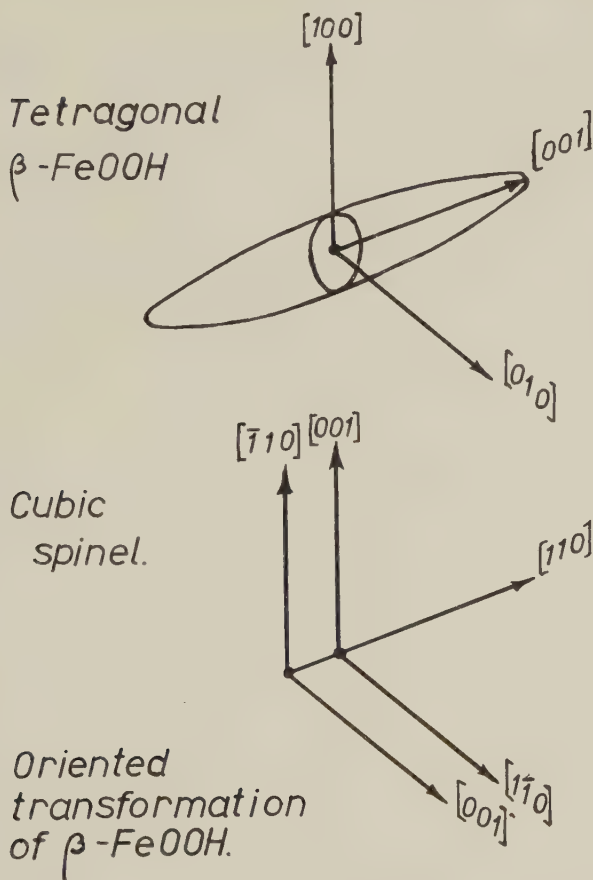


FIG. 10. Diagram of the orientational relationships in the transformation of β -FeOOH.

Single crystals of β -FeOOH have been heated in the beam of the electron microscope and the resulting transformation has been followed by observing the changes in their diffraction patterns. First, the single crystal spot pattern developed streaks along the layers perpendicular to $[001]$ (fig. 8). The 002 reflection became very noticeable and weak intermediate layer lines doubling the c -axis appeared. Mukherjee's observa-

MAGNETITE

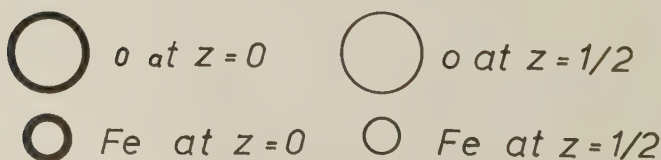
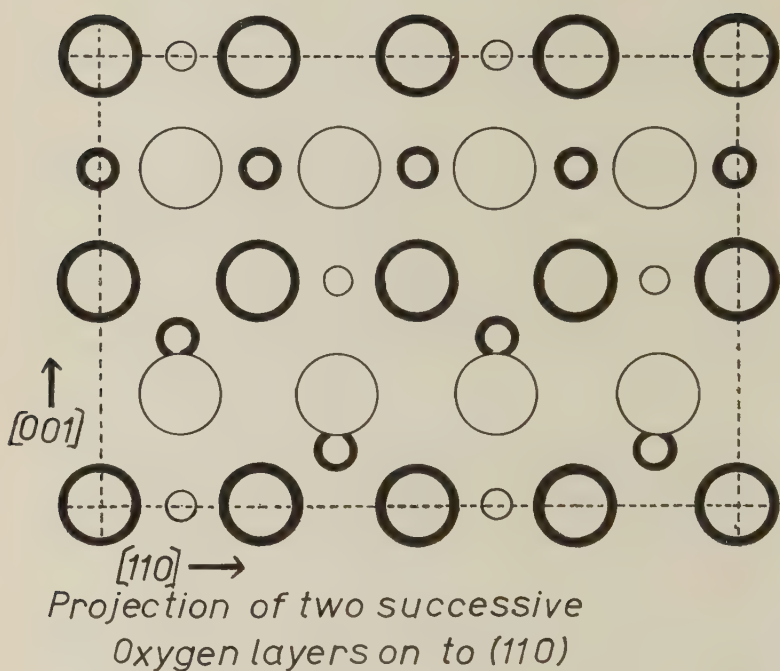


FIG. 11. Plan of a (110)-section through the magnetite structure to show the similarity to the β -FeOOH structure.

tion (1960) of the doubling of the c -axis in hollandite might be recalled in this connexion. The streakiness next cleared and the resulting rectangular pattern (fig. 9) could be indexed as being due to crystals with a spinel structure in two orientations (fig. 10). The two orientations are to be expected as the fourfold axis of β -FeOOH is replaced by a two-fold axis of the cubic phase and by Neumann's principle the overall point group symmetry cannot be lowered by such a transformation.

The spinel is presumably γ - Fe_2O_3 although reduction to Fe_3O_4 under the very low oxygen pressure conditions in the microscope cannot at present be excluded.

The exothermic peak observed by Mackenzie in the d.t.a. curve of the dehydration of β - FeOOH may then be the γ - Fe_2O_3 to α - Fe_2O_3 transformation which releases about 8 kcal./mol.

Examination of fig. 11 shows the similarity between a section through the spinel structure parallel to (110) and the β - FeOOH structure. Only the migration of Fe ions to tetrahedral sites and an expansion of the O-O distance from 3.49 to 4.17 Å. in one direction and a contraction from 3.49 to 2.95 Å. in a perpendicular direction are necessary and these may follow from the migration of the iron.

Acknowledgements are due to my colleague Dr. D. R. Dasgupta for his help during this investigation and for many useful observations. The work described forms part of a research programme on magnetic ores sponsored by the Department of Scientific and Industrial Research to whom we are grateful for financial support.

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The biaxial ray surface.

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[Read 31 March 1960.]

Summary. Existing descriptions of the biaxial ray surface are, in general, misleading. A more accurate description, stressing the simplicity of the surface, is proposed and this is supported by numerous sections drawn through or near the singular points.

TO the mathematician, the equation to the ray surface (Fresnel, 1827, p. 138)

$$a^2x^2(b^2-r^2)(c^2-r^2)+b^2y^2(a^2-r^2)(c^2-r^2)+c^2z^2(a^2-r^2)(b^2-r^2)=0 \quad (1)$$

indicates one continuous surface whose configuration is indicated exactly and in every detail by the equation (e.g. Bell, 1926, pp. 267-269). To those who are less mathematically competent, including the ordinary student of crystal optics, such an equation has little meaning: students in this category must rely upon published sections and written descriptions for their impressions of the surface.

Most published sections of the biaxial ray surface tend to give one the impression that it consists of two surfaces, one totally enclosed within the other, in contact with each other at four points; published verbal descriptions do little to erase this misconception.

The methods used by different authors to describe the ray surface fall in general into three categories (purely analytical unillustrated treatments are not considered):

Analytical or non-analytical treatment in three coordinate planes, usually with illustration of these three planes; e.g. Fletcher (1892, pp. 32-35) and Born (1933, pp. 234-238).

Analytical or non-analytical treatment of three principal planes supported by three-dimensional representation showing all three planes, but with virtually no verbal description; e.g. Eskola (1946, pp. 109-110), Groth (1905, pp. 91-96; 1910, pp. 129-135), Joos (1934, pp. 357-358), Liebisch (1896, pp. 357-358), Miers (1929, pp. 159-160), Nye (1957, p. 240), Rogers and Kerr (1942, pp. 99-101), Schulz (1928, p. 472), Tunell (1933, pp. 335-336), and Wahlstrom (1949, pp. 124-128). In addition, Joos (1934, fig. 3, plate 1) provides a photograph of a well-made solid model of the ray surface depicting, in one octant, the inner sheet and, in the adjacent octant, the outer sheet. The continuity of both sheets through the singular point is

suggested by several continuous lines on the surface, all of them passing through the singular point; but attention is not drawn to this most important feature of the surface.

Third, usually as in the second method plus a verbal description of the configuration of the surface in three dimensions; for example:

Basset (1892, p. 120): "... the wave surface ... consists of an outer and an inner sheet, which intersect at four points in the plane xx ."

Courant and Hilbert (1937, p. 459): "Danach ist die Strahlenfläche eine Fläche derselben Art wie die Normalenfläche . . ." and "Die Strahlenfläche zerfällt genau wie die Normalenfläche in zwei Mäntel. . . ." Of the "Normalenfläche" they say (*ibid.*, p. 458): "Der äußere Mantel . . . besitzt in den vier Doppelpunkten vier nach innen gerichtete konische Ecken, während dort der innere Mantel nach außen gerichtete konische Ecken hat."

Drude (1902, p. 327): "This surface, like the normal surface, consists of two sheets. These two surfaces are very similar to each other. . . ." Of the normal surface he says (*ibid.*, p. 318): "In the xz -plane . . . the two sheets of the normal surface intersect. It can be shown that *this occurs for no other directions of the wave-normal*."

Houstoun (1921, p. 208): "The wave surface . . . consists of two sheets which meet in four points . . . and nowhere else."

Jenkins and White (1953, p. 517): "The outer surface of the complete wave surfaces touches the inner at only four points, where it forms 'dimples'." In addition, in their sections, the inner and outer portions of the surface are divorced by the former being drawn in heavy lines.

Johannsen (1914, p. 97): "It is a warped surface . . . symmetrical along the three principal axes and having four depressions lying in a single plane."

Pockels (1906, p. 44): "Die Strahlenfläche der zweiachsigen Kristalle ist eine Fläche 4. Ordnung und 4. Klasse. Sie besteht aus zwei Schalen, welche nur in den vier auf den Strahlenachsen liegenden *konischen Doppelpunkten* zusammenhängen."

Tutton (1922, p. 866): "The wave-surface . . . is a surface of the fourth degree composed of two shells, one within the other. These two shells touch each other at four points, which are at the bottom of depressions in the outer shell and on the summits of protuberances on the inner one. . . . Except for these depressions and protuberances where actual contact occurs the two shells resemble ellipsoids of general triaxial form. Indeed it is common to regard the shells as two separate wave-surfaces."

Winchell (1931, p. 152): "... the complete wave-fronts are continuous surfaces intersecting in only four points . . .".

Wölffing (1902, p. 364): "Die Wellenfläche besteht aus *zwei Mänteln*, welche in den Knotenpunkten aneinanderstoßen." (This paper contains a comprehensive bibliography of earlier literature on the subject.)

Wood (1934, p. 377): "The wave-surface . . . consists of two sheets . . ." and (*ibid.*, p. 379) "By a little exercise of the imagination it is easy to see the general form of the inner and outer sheets. . . . The outer sheet has the general form of an ellipsoid with four depressions or pits similar to the pit found on an apple around the point where the stem is inserted, only much shallower. At these four points the two sheets come in contact. . . ."

Givens and Discher (1954, p. 381) carry the description a stage beyond that reached in the foregoing by providing three new sections through and near the singular points. In addition they state (*ibid.*, p. 380): "... considerable point may be made of the fact that the outer and inner sheets of the wave surface meet at only

four points"; and (ibid., p. 381), "It is not easy to imagine two sheets which can 'intersect' so cleanly . . . and yet have only point intersections, i.e., no curves of intersection. The two sheets do not intersect in the sense that two cylindrical surfaces often do, but like two wide angle cones placed one above the other and having their apexes in contact."

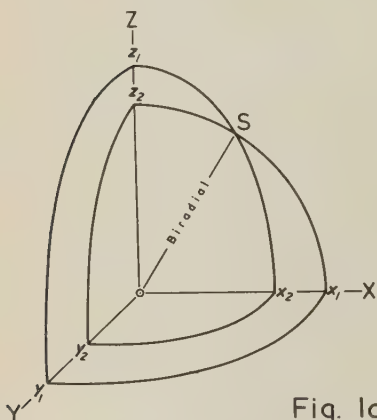


Fig. 1a.

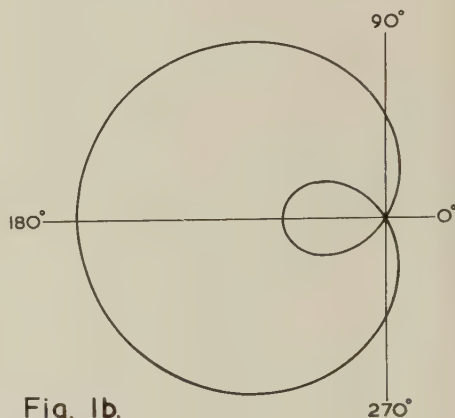


Fig. 1b.

Fig. 1a. Conventional three-dimensional representation of one octant of the ray surface.

Fig. 1b. The Limaçon of Pascal ($r = 1 - 2 \cos \theta$).

Most of the descriptions in the last group have one feature in common: they tend to stress the double nature of the surface and so give the non-mathematician the impression that two surfaces are involved—two surfaces that at the four singular points intersect, touch, zusammenhängen, aneinanderstoßen, come in contact, meet, or even "intersect", according to the individual authors involved.

Rossi (1957, p. 293) gives a less misleading impression: "... the wave front does not consist of two separate surfaces, but of a unique continuous surface folding upon itself and intersecting in a complicated manner".

However, in none of the foregoing papers or texts is attention drawn to the essential simplicity of this extraordinary surface—a property that is to be expected of this, a very special as opposed to a general, case of the fourth degree surface:

It is one continuous surface that intersects itself at the four singular points; the points of intersection divide the surface into two unequal portions of which one is contained wholly within the other.

(The Limaçon of Pascal (fig. 1b), $r = b - a \cos \theta$ where $b < a$ (Walker, 1950, p. 29), is perhaps the simplest two-dimensional analogue).

This simple relationship is easy to visualize if one considers the movement of a free point upon the surface. It is obvious from the standard 3-plane representation of the surface (fig. 1a) that within the three coordinate planes the moving point can neither pass from the outer to the inner portion of the surface nor vice versa without passing through the singular point S .

Consider a possible path $y_1z_1Sx_2y_2z_2Sx_1y_1$ (fig. 1a) for the moving point. Part of this path lies on the outer, part on the inner portion of the surface; but the important point is that, in passing from the outer to the inner portion or vice versa through S , the moving point suffers no abrupt change of direction at S : there is a smooth natural passage through S along an elliptical curve (z_2Sx_1 is actually circular). Moreover, this smoothly effected passage through S from one portion of the ray surface to the other is not a peculiarity of the XZ plane: the transition is equally smoothly effected, still through S of course, regardless of the direction of transit through S and provided that there is no discontinuous change of direction at S .

To illustrate the complete continuity of the outer and inner portions of the ray surface through S a series of partial central sections (figs. 2-5) have been constructed through S in several directions (see accompanying stereogram, fig. 6). The sections have been constructed using Fletcher's (1892, p. 48) equations for the velocities, r_1 and r_2 , of rays in a direction defined by its inclinations, σ_1 and σ_2 , to the biradials OS_1 and OS_2 respectively:

$$\frac{1}{r_1^2} = \frac{1}{a^2} \cos^2 \frac{\sigma_1 - \sigma_2}{2} + \frac{1}{c^2} \sin^2 \frac{\sigma_1 - \sigma_2}{2} \quad (2)$$

$$\frac{1}{r_2^2} = \frac{1}{a^2} \cos^2 \frac{\sigma_1 + \sigma_2}{2} + \frac{1}{c^2} \sin^2 \frac{\sigma_1 + \sigma_2}{2} \quad (3)$$

Obviously the absolute values of a , b , and c are not critical in this connexion and, merely to simplify computation, the values 2, 1.5, and 1 respectively have been used throughout. Hence, from the equation (Fletcher, 1892, p. 35)

$$\tan \frac{1}{2} S_1 S_2 = \frac{c\sqrt{(a^2 - b^2)}}{a\sqrt{(b^2 - c^2)}} \quad (4)$$

the angle $S_1 S_2$ between the two biradials, measured across Z (fig. 1), is $61^\circ 13'$.

The values of σ_1 and σ_2 for any chosen ray direction OR within any



Fig. 2.

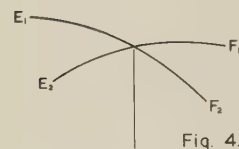


Fig. 4.

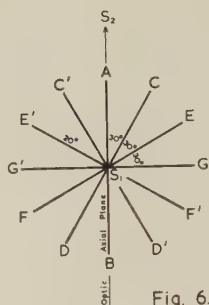


Fig. 6.



Fig. 3.

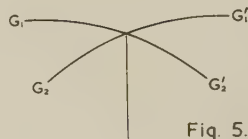


Fig. 5.

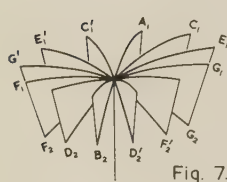


Fig. 7.

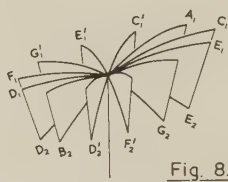


Fig. 8.

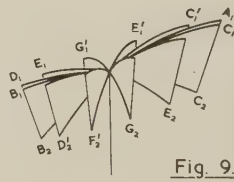


Fig. 9.

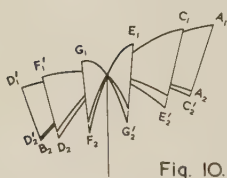


Fig. 10.

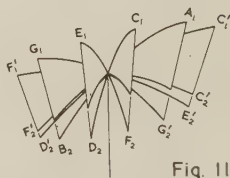


Fig. 11.

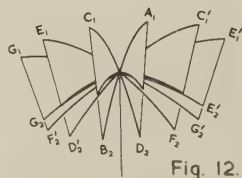


Fig. 12.

FIGS. 2 TO 5. Partial central sections of the ray surface through the biradial, OS_1 (direction represented by vertical line in each case). $A_1 B_1 C_1 \dots$ and $A_2 B_2 C_2 \dots$ are extremities of faster and slower rays respectively traversing directions OA , OB , OC , $\dots$ (see fig. 6).

FIG. 6. Partial stereogram, centre S_1 , showing orientation of sections in figs. 2-5 and 7-12. Section $C'D'$ is symmetrically equivalent to section CD , &c.

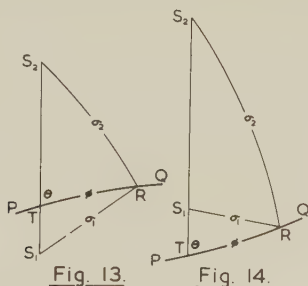
FIGS. 7 TO 12. Three-dimensional representations of that part of the ray surface within 20° of the biradial, OS_1 (direction represented by vertical line in each case), prepared by orthographic projection of figs. 2, 3, 4, 5, and their symmetrical equivalents on a series of planes parallel to the biradial, OS_1 . The projection lines, i.e. lines of sight, are all perpendicular to the biradial, OS_1 , and lie mid-way between the following ray directions (see fig. 6): fig. 7, OB and OD' ; fig. 8, OD' and OF' ; fig. 9, OF' and OG' ; fig. 10, OG' and OE' ; fig. 11, OE' and OC' ; fig. 12, OC' and OA' .

plane of section PQ may then be calculated from the following equations (see stereograms, figs. 13 and 14):

$$\cos \sigma_1 = \cos \phi \cos S_1 T \pm \sin \phi \sin S_1 T \cos \theta \quad (5)$$

$$\cos \sigma_2 = \cos \phi \cos S_2 T \pm \sin \phi \sin S_2 T \cos \theta \quad (6)$$

where $\phi = TR$ = inclination of rays Or_1 and Or_2 to intersection of optic axial plane with plane of section, PQ ; θ = angle S_2TR between plane of



FIGS. 13, 14. Partial stereograms, centre S_1 , showing derivation of equations (5) and (6).

section PQ and optic axial plane; $S_1S_2 = 61^\circ 13'$; $S_2T = 61^\circ 13' \pm S_1T$. For special cases, equations (5) and (6) may be modified as follows:

When $\theta = 90^\circ$:

$$\cos \sigma_1 = \cos \phi \cos S_1T;$$

$$\cos \sigma_2 = \cos \phi \cos S_2T.$$

When $S_1T = 0^\circ$:

$$\cos \sigma_1 = \cos \phi, \text{ so } \sigma_1 = \phi;$$

$$\cos \sigma_2 = \cos \phi \cos S_1S_2 \pm \sin \phi \sin S_1S_2 \cos \theta.$$

When $\theta = 90^\circ$ and $S_1T = 0^\circ$:

$$\cos \sigma_1 = \cos \phi, \text{ so } \sigma_1 = \phi;$$

$$\cos \sigma_2 = \cos \phi \cos S_1S_2.$$

When $\theta = 0^\circ$:

$$\cos \sigma_1 = \cos \phi, \text{ so } \sigma_1 = \phi;$$

$$\cos \sigma_2 = \cos \phi \cos S_1S_2 \pm \sin \phi \sin S_1S_2 = \cos (S_1S_2 \pm \phi)$$

$$= \cos (S_1S_2 \pm \sigma_1), \text{ so } \sigma_2 = S_1S_2 \pm \sigma_1.$$

In addition, partial central sections (figs. 15 and 16) have been constructed perpendicular to the plane S_1S_2 and crossing it 5° on either side of S_1 (see accompanying stereogram, fig. 17). These serve to illustrate that a point on the surface, although moving close to a singular point,

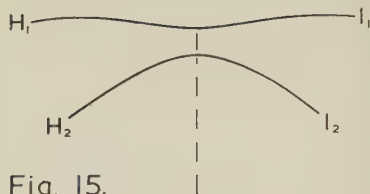


Fig. 15.

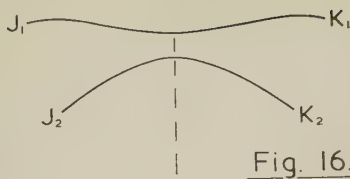


Fig. 16.

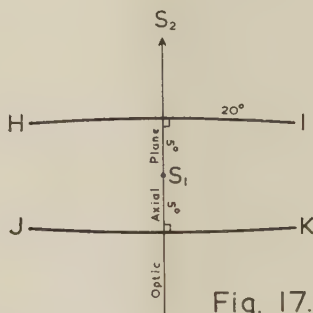


Fig. 17.

FIGS. 15, 16. Partial central sections of the ray surface, crossing the optic axial plane (broken vertical line) 5° each side of the biradial, OS_1 (see fig. 17).

FIG. 17. Partial stereogram, centre S_1 , showing orientation of sections in figs. 15 and 16.

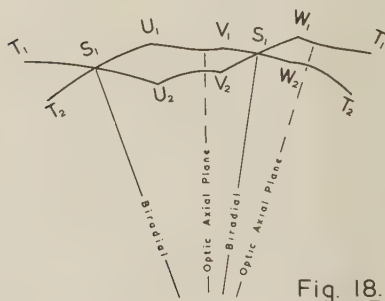


Fig. 18.

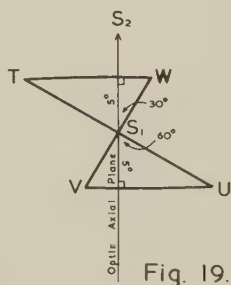


Fig. 19.

FIG. 18. Serial section of ray surface passing twice through and twice near the biradial, OS_1 (see fig. 19).

FIG. 19. Partial stereogram, centre S_1 , showing orientation of serial section in fig. 18.

cannot pass from the outer to the inner portion of the surface or vice versa without passing exactly through the singular point. This is further illustrated by combining several of the foregoing sections in a serial section (fig. 18) passing twice through and twice near the point S_1 (see accompanying stereogram, fig. 19).

Finally, the sections in figs. 2-5 have, by orthographic projection on a series of planes parallel to the biradial, been combined in a series of

diagrams (figs. 7–12) which show in some detail the complete continuity in three dimensions of the inner and outer portions of the ray surface through any singular point.

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A thermal study of thaumasite.

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[Taken as read 2 June 1960.]

Summary. A differential thermal analysis curve of thaumasite shows an endothermal peak at 206° C., corresponding to the loss of H₂O and CO₂, and a weak exothermal peak at 709° C., corresponding to recrystallization to a mixture of anhydrite and larnite, as is shown by X-ray powder photographs of material heated to 950° C. Improved powder data for thaumasite are given: the three strongest lines are at 9.66, 3.79, and 4.58 Å., and the cell-dimensions are a 10.992, c 10.311 Å.

THE sample of thaumasite used in this work is from Bull Runn Quarry, Centerville (Virginia), and was put at our disposal by R. A. Highbarger. It is a paragenesis of this mineral with apophyllite and a chlorite identified as pennine. The apophyllite occurs in large tetragonal crystals, which are transparent and colourless to light green; they are well formed, with {100} and {001} only, and the pennine occurs as small grains or as a dark green film covering them.

Among the apophyllite crystals is a very pure white mass of thaumasite formed by a great number of little crystals, of an average size $0.280 \times 0.048 \times 0.033$ mm., which as seen under the microscope are completely transparent and colourless; they are well formed, of prismatic, almost acicular habit, in which the faces of the prism are observed (figs. 1–3). They are not pleochroic, with straight extinction, low refraction, and moderate birefringence (0.039).

The indexed powder data for thaumasite, obtained with Cu-K α radiation in a 229.2 mm. diameter camera of the Guinier-DeWolff type, is given in table I; intensities were measured with an integrating microphotometer. The indexing is based on a unit cell with a 10.992, c 10.311 Å.; previous values are: a 10.90, c 10.29 Å., Aminoff (1933); a 10.95, c 10.30 Å., Welin (1956); a 11.03, c 10.40 Å., Knill (1960). The three strongest lines of the powder photograph are 9.66, 3.792, and 4.582 Å.

A differential thermal analysis of the thaumasite has been made with the apparatus of the Inorganic Chemical Laboratory at the Faculty of Science, University of Barcelona.



FIG. 1 (*left*): Specimen of thaumasite, with apophyllite and pennine. The white mass among the tetragonal prisms is the thaumasite.

FIG. 2 (*right*): Crystals of thaumasite; approximately $\times 20$.

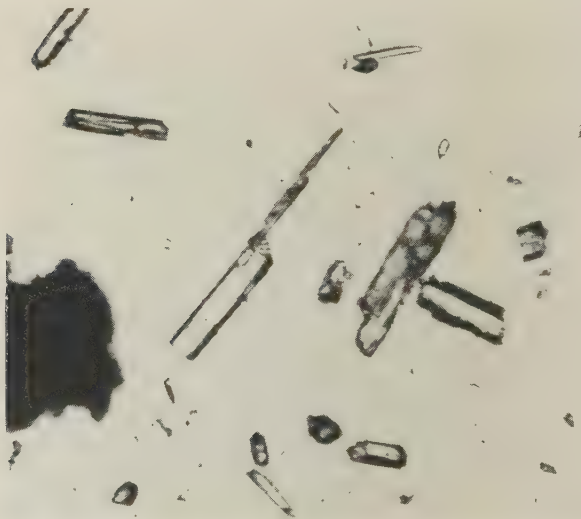


FIG. 3. Crystals of thaumasite; the top left-hand part of fig. 2 at a higher magnification, approx. $\times 80$.

TABLE I. Indexed X-ray powder data for thaumasite from Bull Runn Quarry, Centerville, Virginia, U.S.A. Cu- $K\alpha$ radiation, camera diameter 229.2 mm. Indexed on cell-dimensions a 10.992, c 10.311 Å.

d , Å.	I .	hkl .	d , Å.	I .	hkl .	d , Å.	I .	hkl .
9.66	100	1000	2.0110	18	$\begin{cases} 32\bar{5}2 \\ 10\bar{1}5 \end{cases}$	1.5598	3	$\begin{cases} 60\bar{6}1 \\ 43\bar{7}0 \\ 40\bar{4}5 \end{cases}$
7.075	12	10 $\bar{1}1$	2.0010	9	30 $\bar{3}4$			$\begin{cases} 43\bar{7}1 \\ 21\bar{3}6 \end{cases}$
5.535	44	11 $\bar{2}0$	1.9500	3	40 $\bar{4}3$	1.5431	4	$\begin{cases} 52\bar{7}0 \\ 51\bar{6}3 \end{cases}$
5.221	6	0002	1.9285	10	41 $\bar{5}2$	1.5384	3	$\begin{cases} 50\bar{5}4 \\ 42\bar{6}4 \end{cases}$
4.889	18	$\begin{cases} 20\bar{2}0 \\ 11\bar{2}1 \end{cases}$	1.9200	7	11 $\bar{2}5$			$\begin{cases} 61\bar{7}0 \\ 52\bar{7}2 \end{cases}$
4.582	65	10 $\bar{1}2$	1.9070	7	50 $\bar{5}0$	1.4580	9	$\begin{cases} 22\bar{4}6 \\ 43\bar{7}3 \end{cases}$
4.355	10	20 $\bar{2}1$	1.8945	9	20 $\bar{2}5$	1.4222	6	$\begin{cases} 51\bar{6}4 \\ 44\bar{8}0 \end{cases}$
3.792	75	11 $\bar{2}2$	1.8785	1	$\begin{cases} 50\bar{5}1 \\ 22\bar{4}4 \end{cases}$	1.4715	4	$\begin{cases} 61\bar{7}2 \\ 52\bar{7}3 \end{cases}$
3.623	4	21 $\bar{3}0$			$\begin{cases} 33\bar{6}0 \\ 32\bar{5}3 \end{cases}$	1.3914	3	$\begin{cases} 40\bar{4}6 \\ 70\bar{7}0 \end{cases}$
3.529	31	20 $\bar{2}2$	1.8430	6	31 $\bar{4}4$	1.3757	1	$\begin{cases} 53\bar{8}0 \\ 44\bar{8}1 \end{cases}$
3.422	36	21 $\bar{3}1$			$\begin{cases} 42\bar{6}0 \\ 33\bar{6}1 \end{cases}$			$\begin{cases} 33\bar{6}5 \\ 42\bar{6}5 \end{cases}$
3.263	20	10 $\bar{1}3$	1.7990	8	50 $\bar{5}2$	1.3655	4	$\begin{cases} 70\bar{7}1 \\ 53\bar{8}1 \end{cases}$
3.188	15	30 $\bar{3}0$			$\begin{cases} 41\bar{5}3 \\ 21\bar{3}5 \end{cases}$	1.3550	2	$\begin{cases} 60\bar{6}4 \\ 32\bar{5}6 \end{cases}$
2.981	4	21 $\bar{3}2$			42 $\bar{6}1$	1.3415	1	61 $\bar{7}3$
2.935	10	11 $\bar{2}3$	1.7892	10	40 $\bar{4}4$	1.3384	1	43 $\bar{7}4$
2.756	3	22 $\bar{4}0$			51 $\bar{6}0$	1.3303	1	44 $\bar{8}2$
2.714	37	30 $\bar{3}2$			0006	1.3227	3	$\begin{cases} 62\bar{8}0 \\ 41\bar{7}6 \end{cases}$
2.6465	6	31 $\bar{4}0$	1.7666	8	33 $\bar{6}2$			
2.5950	39	0004	1.7480	4	51 $\bar{6}1$			
2.5630	18	31 $\bar{4}1$			42 $\bar{6}2$			
		$\begin{cases} 22\bar{4}2 \\ 21\bar{3}3 \end{cases}$	1.7205	45	10 $\bar{1}6$			
2.4965	66	10 $\bar{1}4$			11 $\bar{2}6$			
2.3571	11	31 $\bar{4}2$	1.6920	20	$\begin{cases} 51\bar{6}2 \\ 31\bar{4}5 \end{cases}$			
2.2770	10	20 $\bar{2}4$			33 $\bar{6}3$			
2.1885	8	32 $\bar{5}0$	1.6410	11	41 $\bar{5}4$			
2.1546	41	40 $\bar{4}2$			20 $\bar{2}6$			
2.1421	18	$\begin{cases} 32\bar{5}1 \\ 22\bar{4}3 \end{cases}$	1.6254	8	42 $\bar{6}3$			
		$\begin{cases} 31\bar{4}3 \\ 21\bar{3}4 \end{cases}$	1.6152	11	60 $\bar{6}0$			
2.1012	22	41 $\bar{5}0$						
2.0665	6	41 $\bar{5}1$	1.5822	3				
2.0495	4							

The d.t.a. curve obtained is reproduced in fig. 4. An endothermic peak appears clearly defined at 206° C., beginning between 135° and 140° C. and finishing between 255° and 260° C. The peak height or amplitude is 155 μ V, with a peak width 120° C. and a slope ratio 1.5. The latter is typical and can be used for identification of minerals of the same group as has been shown by Bramao *et al.*¹ Another peak of exothermic character, little intensity, and symmetrical form is situated at 709° C. It has a peak width 46° C., a peak height 6 μ V, and a slope

¹ L. Bramao, J. G. Cady, S. B. Hendricks, and M. Swerlow, *Soil Science*, 1952, vol. 73, p. 275.

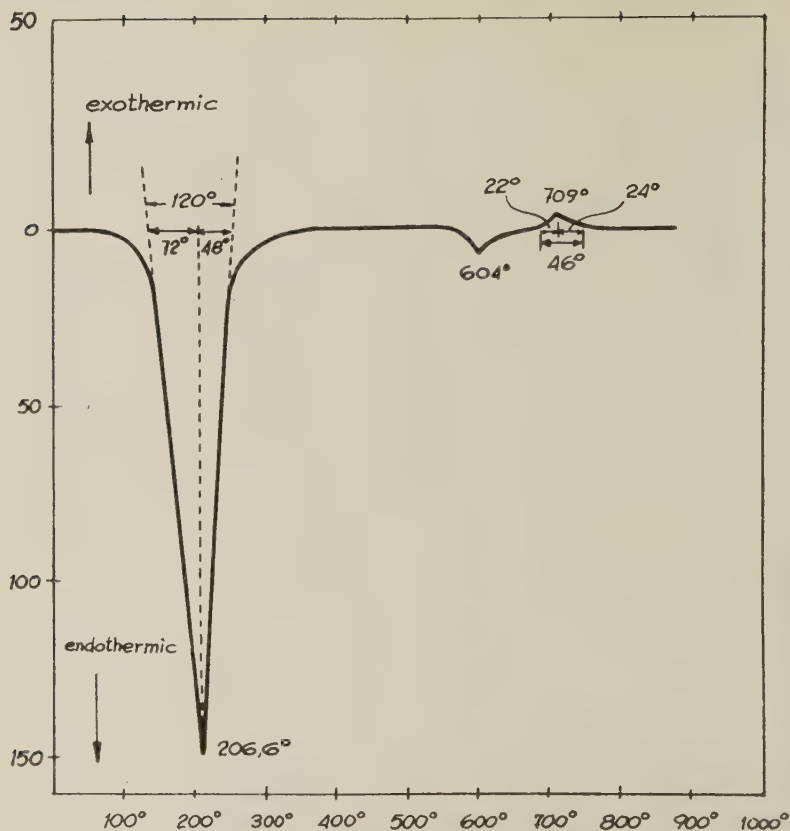


FIG. 4. Differential thermal analysis curve of thaumasite.

ratio 0.92. The endothermic peak situated at 604° C. arises from small quantities of pennine present as an impurity.

The ratio between the two peaks is 7:1 which shows that in the first reaction a quantity of heat is absorbed seven times greater than the one set free in the second. The first peak corresponds to a chemical reaction of first order, whereas the second indicates the consolidation or inversion of a phase.

Previous workers have shown that on heating thaumasite at 205° C. it loses weight by 41.9 %, and at 240°–250° C. loses 43.35 %; the loss continues to increase up to 50.8 % at 330° C. From this temperature up to 1 000° C. no further loss of weight is observed.

These temperatures correspond to the great endothermic peak at 206° C., while the exothermic one of small intensity at 709° C. does not correspond to any loss of weight of the sample.

From this can be deduced: that the first peak corresponds to a chemical reaction of the first order, of an endothermic type, as it is the loss of the 15 molecules of water coordinated with Ca, whose total elimination takes place at a temperature situated on its ascendent branch; owing to the disposition of the CO_3 groups, joined to the rest of the structure by hydrogen bonds through the water molecules, these groups decompose during this period, releasing CO_2 , the material remaining completely without H_2O and CO_2 at about 300° C. And that the second peak, seven times smaller than the first one and of an exothermic type, is due to the consolidation or inversion of a phase.

In order to know the exact happenings, a study has been made of the final phases that are formed when the mineral is heated over 900° C. and below 1 000° C.

X-ray study on thermal decomposition of thaumasite. A sample of thaumasite was heated at 950° C. and analysed by X-ray. In the powder diagrams obtained, two phases have been identified: CaSO_4 (anhydrite) and $\beta\text{-Ca}_2\text{SiO}_4$ (larnite), by means of the A.S.T.M. X-ray powder data file, cards nos. 6-0226, 3-0753, and 3-0761. The data obtained from the sample and the standard data for CaSO_4 and $\beta\text{-Ca}_2\text{SiO}_4$ are reproduced in table II.

During the past few years several attempts have been made to work out the structure of thaumasite. Brú and collaborators (1954, 1957) have presented a possible scheme of structure.

Simultaneously, E. Welin (1956) has proposed a structure for the mineral, using a sample from Långban, Sweden. He accepts the existence of chains $-\text{SiO}_4-\text{Ca}-\text{SiO}_4-\text{Ca}-\text{SiO}_4-$ situated along the *c*-axis, with Ca surrounded by six oxygens, lying at the vertex of a distorted octahedron, three of them belonging to SiO_4 and the other three to water molecules. The groups SO_4 and CO_3 would be linked by hydrogen bonds to H_2O of the octahedron, without direct bonding to the Ca.

The formation of CaSO_4 in the thermal treatment of the mineral seems to be in contradiction with the positions of SO_4 groups in the structure deduced by Welin (1956). In this structure the SO_4 is linked with calcium through a water molecule, which coordinates with calcium without any electric charge and links with SO_4 by a hydrogen bond. Also, in this structural scheme, all the calciums are rigidly joined to chains of SiO_4 . If this were true, one would expect that the final product of the

thermal treatment of the mineral should be only Ca_2SiO_4 , the SO_4 groups being expelled like the CO_3 groups.

TABLE II. X-ray powder data of heated thaumasite and its interpretation.

Thaumasite heated to 950° C.		CaSO ₄ — A.S.T.M. card 6-0226			β -Ca ₂ SiO ₄ —A.S.T.M.			
<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .	<i>hkl</i> .	card 3-0753		card 3-0761	
					<i>d</i> , Å.	<i>I</i> .	<i>d</i> , Å.	<i>I</i> .
3.466	100	3.498	100	$\begin{Bmatrix} 002 \\ 020 \end{Bmatrix}$				
3.072	35				3.06	10	3.04	50
2.856	40	2.849	33	210	2.88	10		
2.788	40				2.78	100	2.76	100
2.740	35				2.74	60	2.71	50
2.699	30				2.67	60	2.67	50
2.329	20	2.328	22	$\begin{Bmatrix} 202 \\ 220 \end{Bmatrix}$				
2.273	20				2.27	40	2.26	50
2.210	20	2.208	20	212				
2.171	30				2.18	80	2.18	75
2.032	15				2.02	20	2.03	50
1.998	20				1.97	20	1.98	75
1.865	30	1.869	15	230	1.89	10	1.89	50
1.800	15				1.79	10	1.80	50
1.743	20	1.749	11	040				
		1.748	10	004	1.70	10	1.70	25
1.648	20	1.648	14	232	1.62	20	1.63	60
1.580	7				1.56	10	1.57	25
1.530	7				1.53	20	1.52	25
1.491	7				1.48	20	1.48	25

The formation of the β -Ca₂SiO₄ explains the appearance of the peak at 709° C. This silicate is stable between 670° C. and 1 420° C.; it may be supposed that after the elimination of the water and CO₂ of the mineral, the phase CaSO₄ becomes consolidated, while the Ca₂SiO₄ remains in the γ -form or in some amorphous state, which could crystallize into β -Ca₂SiO₄ starting at 673° C. This temperature agrees with the starting temperature of the peak.

Acknowledgements. I thank Professors DeWolff and Coronas for permission to work in their laboratories, and Dr. Pujol for helping me in obtaining the d.t.a. curve.

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The following references are additional to the bibliography of thaumasite given by T. VOGT, Norsk. Geol. Tidsskr., 1938, vol. 18, p. 291, and those cited by D. C. KNILL, Min. Mag., 1960, vol. 32, p. 416.

BRÚ (L.), CUBERO (M.), and PEREZ RODRIGUEZ (M.), 1954. An. Real Soc. Españ. Fis. Quim., ser. A, vol. 50, p. 105.

— — — and LOPEZ (A.), 1957. Ibid., vol. 53, p. 67.

Magnetic susceptibility of garnet.

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[Taken as read 2 June 1960.]

Summary. The mass susceptibility of 23 analysed or partially analysed garnets has been measured by means of a calibrated Franz Isodynamic magnetic separator. Straight lines are fitted to the adjusted data for mass susceptibility and molecular composition. The mass susceptibilities of the theoretical end-members in electromagnetic units $\times 10^6$ are estimated as: almandine, 68 ± 2 e.m.u.; spessartine, 81 ± 3 e.m.u.; and andradite, 49 ± 3 e.m.u. Grossular and pyrope are assumed to have susceptibilities of nil.

ALTHOUGH with the increasing use of the isodynamic magnetic separator it has become more obvious that the magnetic susceptibility of ferromagnesian minerals varies considerably with their composition, only in the last few years have attempts been made to correlate these factors. The magnetic data in this paper were obtained with an unadapted laboratory separator during an entirely different research project,² nevertheless the results indicate that under suitable conditions magnetic susceptibility is comparable in accuracy with density for use either as a variable for the estimation of composition or as the basis of a method for the separation of garnets of fixed composition.

Method of investigation. Six of the samples were obtained in the form of analysed powders and the magnetic susceptibility of these was measured without further treatment. The other samples were prepared by crushing to pass 120 mesh, washing to remove dust, and then removing impurities by means of heavy liquids and the magnetic separator. Purity was checked by microscopic examination.

After the determination of the magnetic susceptibility portions of the samples were analysed for total iron, manganese, magnesium, and calcium by an adaptation of the rapid method of Shapiro and Brannock.³ The results for iron and manganese are considered to have a coefficient

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² M. J. Frost, unpublished Ph.D. thesis, 1957, University of Western Australia.

³ L. Shapiro and W. W. Brannock, U.S. Geol. Surv. Bull., 1952, No. 165, and 1956, No. 1036-C.

of variation of about 1 % and those for lime and magnesia a standard deviation of about 0.1 %. All analyses were checked by partial summation and by the comparison of the measured and calculated densities and refractive indices.

Magnetic susceptibility was obtained by measuring, on a standard Franz Isodynamic magnetic separator at constant slope and tilt, the amperage at which the sample was divided into two equal fractions (the critical amperage) and applying the formula $\chi = c/I^2$ where χ is the mass susceptibility in electro-magnetic units, I is the critical amperage, and c is a constant characteristic of the instrument in use. This formula has been independently derived both by Tillé and Kirkpatrick¹ and by McAndrew.²

The value of the constant was obtained by measuring the critical amperage for manganese sulphate and ferrous ammonium sulphate, for both of which the susceptibility is known, and substituting in the formula. Slightly greater accuracy was obtained for the critical amperage by measuring it at several different tilts, plotting the values against the sines of the angles of tilt, and reading the required value from the free-hand fitted curve. For the instrument used the constant had a value of 6.2×10^{-6} .

All measurements were made with a slope of 20° , a tilt of 15° , and a feeding speed of 0.5 c.c./min. Although an unadapted instrument was used considerable care was used in reading the amperage and it is believed that readings were reproducible to 0.01 amp. For a mineral of mass susceptibility of 50×10^{-6} e.m.u. this gives a value correct to $\pm 5\%$, the error decreasing with increasing susceptibility.

Results. The regression lines for magnetic susceptibility on molecular composition were separately determined for each of the three series: pyrope-almandine, almandine-spessartine, and grossular-andradite. The data are given in table I.

In the pyrope-almandine series only the data for those garnets with less than 5 % (molecular) spessartine plus andradite were used. For the purpose of calculation both spessartine and andradite were added to the almandine percentage and both pyrope and grossular were considered to have $\chi = 0$. The regression coefficient of mass susceptibility in e.m.u. on molecular percentage almandine was found to be $(0.69 \pm 0.02) \times 10^{-6}$ (standard error based on 14 observations). The distribution of the

¹ R. Tillé and W. Kirkpatrick, *Zeits. Erzbergbau Metallhüttenwesen*, 1955, vol. 8, Suppl. p. B. 117.

² J. McAndrew, *Proc. Australian Inst. Mining Eng.*, 1957, No. 181, p. 59.

TABLE I. Magnetic susceptibility, χ , of garnets (e.m.u.).

Number.	Occurrence.	Composition (mol. %)					χ $\times 10^6$
		Pyr.	Alm.	Spess.	Gross.	And.	
UWA 37815	Biotite gneiss	29.4	70.0	0.6	0.0	—	46.6
UWA 35719	Cordierite gneiss	24.9	72.0	1.6	1.5	—	54.7
UWA 36159	Cordierite gneiss	20.1	75.1	2.4	2.4	—	48.8
UWA 36337	Garnet granulite	18.5	60.6	1.5	19.4	—	46.6
UWA 25447	Cordierite gneiss	18.0	74.6	4.0	3.4	—	51.6
UWA 37813	Hornblende gneiss	17.2	76.7	1.0	4.1	—	51.6
UWA 36175	Anthophyllite schist	16.6	60.5	1.9	21.0	—	51.6
UWA 37937	Hornblende granulite	11.5	64.7	3.3	20.5	—	62.9
UWA 36336	Secretion pegmatite	9.9	80.3	3.2	6.6	—	54.7
UWA 35274	Garnet gneiss	9.9	83.0	2.5	4.6	—	58.3
UWA 37933	Eclogite	9.8	57.1*	1.3	31.8*	—	39.6
UWA 25370	Hypersthene gneiss	7.7	73.9	2.8	15.6	—	54.7
UWA 36335	Garnet granulite	5.7	85.8	4.1	4.4	—	58.3
UWA 32217	Hornblende gneiss	5.1	70.8	4.3	19.8	—	46.6
UWA 37812	Biotite schist	5.6	85.0	8.6	0.8	—	70.6
UWA 32231	Biotite gneiss	6.6	75.7	14.1	3.6	—	66.1
UWA 36338	Intrusive pegmatite	0.0	64.9	34.8	0.3	—	75.6
GCL 359/28	?	0.2	49.1	50.5	0.2	—	75.6
GCL 2382/32	?	0.3	16.0	78.7	0.0	3.3†	75.6
GCL 1160/26	?	0.8	9.5	87.3	2.4	0.0	75.6
GCL 428/28	?	1.9	3.2	0.2	81.0	13.7	11.5
GCL 3554/32	?	0.2	4.1	0.9	58.0	36.8	24.2
GCL 809/28	?	0.0	0.7	0.5	0.0	98.8	48.8

* Probably includes significant andradite.

† Also 1.7 % quartz.

UWA Catalogue number in the collection of the Geology Department of the University of Western Australia. All analyses by the author.

GCL Catalogue number in the collection of the Government Chemical Laboratory, Perth, Western Australia. Analysts: 359/28, 2382/32, and 809/28, C. R. LeMesurier; 1160/26 and 428/28, E. S. Simpson; 3554/32, D. G. Murray.

values of χ /(mol. % almandine) is skew with a mean, median, and mode of 0.70, 0.66, and 0.65, all $\times 10^{-6}$, respectively. The regression coefficient calculated only on those 10 samples in which χ /(mol. % almandine) does not differ from the mean by more than three times the standard deviation is 0.68×10^{-6} . Since it is believed that most of the anomalies are due to the presence of sub-microscopic inclusions of magnetite with an effective susceptibility possibly greater than that of the garnet by a factor of 10^4 , the lower value is more likely to be accurate. This gives a mass susceptibility for pure almandine of $(68 \pm 2) \times 10^{-6}$ e.m.u.

In the almandine-spessartine series only the data for those garnets with less than 15 % of pyrope plus grossular, less than 5 % andradite, and more than 10 % spessartine were used. The measured magnetic

susceptibilities were corrected on the assumption that pyrope, grossular, and quartz as an impurity have $\chi = 0$. Andradite was added to the almandine percentage and almandine was taken as having $\chi = 68 \times 10^{-6}$ e.m.u. The regression coefficient of corrected mass susceptibility on molecular % spessartine is found to be $(0.13 \pm 0.02) \times 10^{-6}$ (5 samples). The low standard error, despite the corrections, may be partly due to the high purity of the mainly pegmatitic garnets, but the low number of spessartine-rich garnets in the sample precludes high accuracy. If this value is accepted the mass susceptibility of pure spessartine is 81×10^{-6} e.m.u. The high susceptibility of spessartine compared with almandine is fully in accord with the ionic susceptibility of manganese and with the results¹ on wolframite.

In the grossular-andradite series only the data for specimens with less than 5 % almandine plus spessartine were used. The measured magnetic susceptibilities were corrected on the assumption that almandine and spessartine have the susceptibilities already obtained. The mass susceptibility of grossular was experimentally determined to be less than 10^{-6} e.m.u. and it is assumed for the purpose of calculation to be nil. The regression coefficient of corrected mass susceptibility on molecular percentage andradite is 0.49×10^{-6} (3 samples). Although the number of samples is small the value of 49×10^{-6} e.m.u. for the mass susceptibility of pure andradite is probably at least as accurate as that for spessartine.

Acknowledgements. My thanks are due to Prof. R. T. Prider and Dr. A. F. Wilson for their encouragement and assistance during the progress of this work. Acknowledgement is also due to the then Director of the Government Chemical Laboratories (Western Australia), H. P. Rowledge, for making available a number of samples of analysed garnet and to Messrs. J. G. Blockley, C. Becker, M. Finucane, and J. H. Francis for the donation of specimens.

¹ E. M. Spokes and D. R. Mitchell, *Mining Engineering* (New York), 1958, vol. 10, p. 373.

SHORT COMMUNICATIONS

Bavenite from the Meldon aplite quarries, Okehampton, Devonshire.

THE Meldon aplite quarries are situated on both banks of the Red-a-ven Brook about $2\frac{1}{2}$ miles south-west of Okehampton on the northern border of Dartmoor. Worth¹ described and illustrated the working on the north side of the brook. Here in a vertical dip section thinly bedded calc flintas dipping at 35° northwards are crossed by four counter-dipping aplite dykes. On the southern side of the quarry the dip of the dykes is 55° , but this decreases to 25° as the northern face is approached. Here both aplite and calc flinta are crossed by a strong joint system inclined sub-parallel to the dyke walls in the southern face, and these have served as channels for pneumatolysis associated with the main Dartmoor granites. Joints within the wall rocks are lined with thin films of axinite, but on entering aplite these spread out as reaction veins up to 2 inches in thickness. The complete mineral assemblage of these veins is axinite, datolite, fluorite, prehnite, calcite, pyrrhotine, quartz, albite, and these frequently project as finely developed crystals into a central fissure.

One narrow fissure was found to be lined with small crystals of quartz, albite, and octahedral fluorite. Filling this cavity at one point was an incomplete rosette of bavenite laths, 5 cm. in diameter. On free surfaces at the margin of the rosette bavenite has crystallized as terminated tablets (fig. 1) projecting radially into the cavity. These crystals are colourless, though the massive material has a pale lilac hue. They attain a length of 6 mm., and a width of up to 2 mm., are set with the largest



FIG. 1. A typical crystal of bavenite from the Meldon aplite quarries, Okehampton.

¹ R. H. Worth, *Quart. Journ. Geol. Soc.*, 1919, vol. 75, p. 77.

faces normal to the vein walls, and in places are encrusted with other vein minerals. Beyond the margin are parallel growths of doubly terminated rectangular tablets of bavenite from 0.1 to 0.5 mm. in width and up to 1 mm. in length.

The faces observed (fig. 1) have been indexed using the unit-cell dimensions of Claringbull¹ and the orientation of Ksanda and Merwin.² As in the Swiss occurrences described by Claringbull¹ the mineral is elongated parallel to [001] with a perfect cleavage parallel to (100), the largest faces (010) modified by (120) are striated in the direction of the *c*-axis from repetition of the two forms. Crystals are terminated by bright faces of the form (041). The refractive indices α 1.584, β close to α , γ 1.590, optic plane (010), $\alpha - c$ [001], $2V\gamma = 48^\circ$, and $D_4^{19} 2.73$ agree closely with published data.

The identity of the mineral was suggested by preliminary optical examination and confirmed by an X-ray powder photograph. A qualitative spectrographic examination showed calcium, germanium, aluminium, and silicon. Germanium was previously detected in bavenite from the type locality but not in Swiss specimens.¹

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¹ G. F. Claringbull, *Min. Mag.*, 1940, vol. 25, p. 495.

² C. J. Ksanda and H. E. Merwin, *Amer. Min.*, 1933, vol. 18, p. 341 [*M.A.* 5 474].

Relation between square net and Weissenberg net: a visual aid.

A VERY simple, easily constructed device enables one to demonstrate the relationship between the orthodox plane net with rectangular coordinate axes and straight grid-lines and the Weissenberg net with straight, mutually parallel coordinate axes and curved grid-lines. The apparatus consists of a card, on which is drawn a square net, and a cylindrical mirror (fig. 1). The dimensions of the various parts as used in this department are as follows: card 20" $\times$ 20", net 3 cms. square, mirror 5" high $\times$ 1½"

diameter. The dimensions are of course not critical and anything approximating to these values will give the desired result. The grid lines in the two axial directions should by preference be coloured or ruled differently. The mirror is easily constructed by nickel- or chrome-plating a polished brass tube.

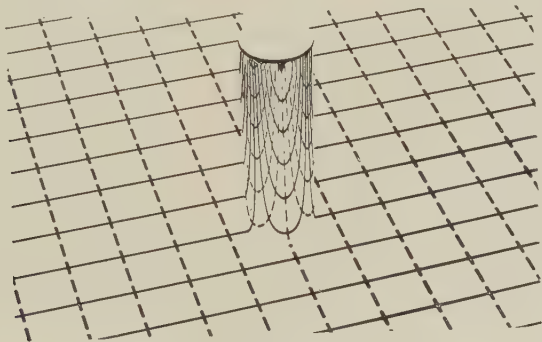


FIG. 1

The cylindrical mirror, when placed at the intersection of the coordinate axes with its axis perpendicular to the plane of the card, presents to the unaided eye an image of the plane square net in which the coordinate axes OX , OY , $O\bar{X}$, $O\bar{Y}$ appear as regularly spaced parallel straight lines, and the grid-lines $x = \pm 1, \pm 2, \dots, \pm n$, $y = \pm 1, \pm 2, \dots, \pm n$ are represented by families of curved lines in the fields limited by the parallel axes OY , $O\bar{Y}$ and OX , $O\bar{X}$ respectively. These are the characteristics of the Weissenberg net. The image presented here and the normal Weissenberg net differ only in the attitude of the coordinate axes: in this visual aid they are perpendicular to the base of the image; in the Weissenberg net they are inclined to the base of the net at an angle depending upon the translation coefficient of the camera used.

Although over most of the mirror field the image is fairly accurate one should, strictly, consider only that part of the image lying in the plane defined by the eye and the mirror-axis: e.g. when the eye:mirror-axis plane does not contain a coordinate axis of the plane net, that axis assumes a slight curvature in the image, especially at the bottom of the mirror and as a consequence does not appear to be parallel to any other axis viewed simultaneously (fig. 1). Thus the ideal complete picture of the Weissenberg-type image should be built up of a continuous series of such partial images viewed from all directions around the mirror. This

may of course be achieved either by the observer moving round the stationary net and mirror or by the net with mirror being rotated about a vertical axis by the stationary observer. Further, the eye should be at such a height above the plane of the card that the image of the card edge is at or above the top of the mirror: the mirror will then be filled by the image.

Small dark disks may be placed on the square net in positions corresponding to those occupied by nodes of any layer of any reciprocal lattice: their corresponding positions on the Weissenberg-type net may then be observed in the mirror.

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BOOK REVIEWS

STASIW (O.). *Elektronen- und Ionenprozesse in Ionenkristallen. Mit Berücksichtigung Photochemischer Prozesse.* Berlin (Springer), 1959. viii+307 pp., 107 text-figs. Price (bound) DM 66.

Volume xxii of the well-known series *Struktur und Eigenschaften der Materie* is written and produced according to the standard expected. There are many books on electronic and ionic conduction and diffusion processes in solid bodies. Professor Stasiw gives a complementary picture concerning photochemical reactions in ionic solids. The aim is to fit photochemical processes into the general picture of defect reactions.

The mathematical treatment adopted is comparatively simple; it deals with statistics of defects in ionic crystals, energy of the lattice and of its defects, diffusion, and ionic conductivity. A simplified picture of the band model for ionic crystals is presented, and the absorption spectra of the real ionic lattice and of the ideal lattice with stoichiometric defects or with added foreign ions are considered. The semi-conduction process is treated in relation to structure, and there are sections on photoelectric conduction. Photochemical processes in pure ionic lattices, in lattices with impurities, and in mechanically deformed crystals are all considered. The subjects treated include photochemical changes in alkali halides irradiated with X-rays and photochemistry of silver halides. A special chapter deals with the relationship between defects and nuclear resonance.

The author has deliberately limited himself to the simplest ionic lattices, and has given a comprehensive account of this. He has achieved this without overloading the text with mathematical difficulties. When necessary, towards the end of the book and in an appendix, he gives appropriate mathematical treatment. Many mineralogists may prefer not to give much attention to this part; the book has been arranged so that those with a more general interest in the properties of crystals need not do so.

H. M. P.

NORTHROP (Stuart A.). *Minerals of New Mexico*. Revised [second] edition. University of New Mexico Press, Albuquerque, 1959, 665 pp., map (16 miles = 1 in. approx.). Price \$10.00.

This is a second and revised edition of the author's former work published in 1942 [M.A. 8-357]. It has been greatly expanded and there are now 665 pages (formerly 387); the page size has been considerably increased and the price has risen from \$1.75 (bound) to \$10.00. Part I, as before, deals with the history and prehistory of New Mexican mineralogy and in addition to the features in the former edition there are sections on minerals discovered since 1925; recent and unpublished records of occurrences; fluorescent minerals and radioactive minerals. The economic aspects of mineral industry in the state have also been brought up to date. Part II, an alphabetical catalogue of minerals, now includes about 440 species and 130 varieties, also many synonyms, some of them purely local names such as "Mora diamond" and "Pecos diamond" (quartz). The localities of each species are given under counties with descriptions of the occurrence and references to the literature. Part III consists of an alphabetical list of districts, subdistricts, camps, &c., and is followed by an extensive bibliography. This excellent reference book represents such a great amount of careful research that it would perhaps be ungracious to wish that the topographical index had been a complete index of the localities mentioned in Part II. This, however, is always the ideal to be aimed at by the topographical mineralogist.

J. M. S.

JUNG (J.) and BROUSSE (R.). *Classification modale des roches éruptives, utilisant les données fournies par le compteur de points*. Paris (Masson et Cie.), 1959. 122 pp., 5 figs., 5 tables. Price 14.00 fr.

This handbook of the quantitative classification and nomenclature of igneous rocks is of interest mainly as an attempt to discard the chemical-

mineralogical system of Lacroix, long a handicap to French petrographers, for one based on modal composition alone. The authors are to be congratulated on this, but they remain slaves to many French conventions, among which are the principle of classifying plagioclase rocks according to the plagioclase first to crystallize, the use of the term "mesocratic" (rightly rejected as nonsensical by Shand), and the preservation, in the index of 492 selected names, of most of Lacroix's terms for local freaks. This last has been carried so far as the creation of a special family to accommodate anabohsite and avezacite.

The scheme adopted is on similar lines to those of Johannsen, of Niggli, of Tröger, and of Hatch, Wells, and Wells, with conventional names applied to a series of "pigeonholes" defined by the usual coordinates (silica-saturation, colour-index, alkali-feldspar in total feldspar, &c.). A series of indices in terms of these coordinates is proposed to define the position of rocks in the system, but some of the indices are calculated and used in such a manner as to render them of little value. For example, the *indice de saturation* is calculated on light minerals alone, treating olivine as saturated and melilite as a feldspathoid; and in the calculation of negative values from feldspathoids the latter are treated as mutually equivalent despite the great difference in the amounts of silica necessary to convert leucite and nepheline to alkali feldspar. The terminology for sub-ranges of these indices is often misleading; for example, rocks with up to 40 % leucite in total feldspathoid are called *roches néphéliniques* as distinct from *roches leucito-néphéliniques*.

There is a praiseworthy but rather inconclusive attempt to deal with the problem of names of different status, corresponding to the concepts of genera, species, and varieties. As so often happens with petrographic systems, the authors have assigned their own arbitrary meanings to many names in actual current use. Their use of essexite, theralite, tephrite, basanite, and tonalite, to take only a few, is novel and arbitrary; and tonalite only fits into its allotted pigeonhole because the composition of its plagioclase is misquoted. Nor is any authority quoted for the indices of composition given for most of the names indexed.

Most quantitative petrographic systems, however, are subject to criticism of the above kind, and the authors also deserve praise on some points. There is a worthy attempt to deal with the nomenclature of palaeovolcanic and glassy rocks. The proposal to use the prefixes leuco-, meso-, and mela- for the leucocratic, mesotype, and melanocratic facies of rock types is sound, provided that it is not applied to the median type concerned.

The classificatory scheme is prefaced by a practical account of the point-counter technique, including rules for the minimization of analytical errors based on the work of Chayes. S. E. E.

VITANAGE (P. W.). *Geology of the country around Polonnaruwa (one-inch geological sheet 47, preliminary series)*. Memoir No. 1, Department of Mineralogy (Geological Survey of Ceylon), 1959. Price Rs. 7.50.

The Department of Mineralogy (Geological Survey) of Ceylon, re-organized in recent years, has planned to publish a series of Memoirs describing the one-inch map sheets of the island and a series of Bulletins covering its various mineral occurrences. These two series are to supersede the Professional Papers, of which two have appeared; this volume is the first Memoir.

The Memoir is predominantly petrological, for Precambrian crystalline rocks underlie the entire map area. Amongst these rocks ancient metamorphosed sediments are prominent. They include quartzites, charnockites of sedimentary aspect, quartz-garnet-sillimanite-graphite-schists (type khondalites), calc-gneisses, and crystalline limestones. As well as these there are microcline-gneisses and migmatitic gneisses with conformable pegmatites. The rocks have been described in five groups, each with distinctive lithological and structural characters.

All the formations have been isoclinally folded with north-south strike, and overturned towards the east (Tabrobanian movements). A later movement with compression at right angles to the first has produced buckling and fracture of the pre-existing folds and NNW.-SSE. (dextral) with NNE.-SSW. (sinistral) tear faults (Vijayan movements). Finally, there are north-south shear zones in which tectonic breccias occur.

Although no ore deposits exist in the area there is abundant and good building stone and lime available, and the ground water conditions of the district are discussed in detail.

The Memoir is well provided with mineralogical and petrological descriptions, chemical analyses, diagrams, and photomicrographs, together with excellent lithological and structural maps. By reason of the quality of this first volume, and because the island is so largely underlain by crystalline rocks, this series of Memoirs ought to be taken by all Institutes wholly or partly devoted to petrology. G. H. F.

MICHEL-LÉVY (CHRISTOPHE). *Tableaux des Minéraux des Roches*. Centre National de la Recherche Scientifique, Paris, 1959. Price: Nf. 12.

This slim Royal 4to paperback publication is the successor to a similar volume, with the same name, by Auguste Michel-Lévy and Alfred Lacroix, published in 1899. It is a key to the identification of certain minerals that can be identified in thin sections of rocks, excluding almost all opaque minerals, water-soluble minerals, and most of the minerals of metalliferous veins.

In a preliminary two-page table the various symmetry systems (with tetragonal to triclinic each split into optically negative and optically positive groups) are read against a series of intervals for the values of maximum birefringence. The pigeonholes of the grid, so constructed, each contain the name or names of minerals appropriate to them, together with the mean refractive index of each mineral. After optical examination, therefore, an unknown mineral is placed within a single pigeonhole by identification of its symmetry and birefringence and tentatively identified with the mineral in that pigeonhole whose mean refractive index most closely agrees with it. The mineral so obtained is then looked up in the second and principal part of the book, namely an alphabetical arrangement of all the minerals covered, with the simplification that mineral families are grouped together under the single entry of the family name. Each mineral entry provides the chemical formula, density, symmetry system, space group, cleavages, &c., optical orientation, $2V$, dispersion, refractive indices, birefringence, crystallographic parameters, and remarks.

This new tabulation will probably be particularly welcomed in France, but perhaps less elsewhere, for so many standard reference books and also tabulations more or less similar to this one are now in use. This volume is, indeed, the last of a long line of such tabulations.

An exhaustive list of minor errata would be impractical and also discourteous in a review of this sort. The tables are, broadly speaking, accurate and certainly of value for students. A few observations do, however, appear worth while. Firstly, the minerals pollucite, gonnardite, rhomb-feldspar (potash oligoclase), stilpnomelane, and various chlorites are omitted. The chlorites included belong to the French classification, but those omitted occur in a later review of the chlorites (Min. Mag. 30-277). Amongst points raised by the optical descriptions one notes the blank space for optic axial dispersion in hambergite, which in fact has appreciable dispersion. Beryllonite $\{010\}$ cleavage flakes give good centred acute bisectrix figures, but the tables state that the optic axes

are parallel to the cleavage. On p. 27 lazurite is a feldspathoid, on p. 26 it is not. The statement that chrysoberyl has $2V = 45^\circ$ is misleading because its optic axial angle is very variable. Garnierite, saponite, sepiolite, and "attapulgitite" are not serpentines. There are a few definite spelling errors, such as "ashkroftine" (p. 6), "corundophyllite", "saphirine", "xantophyllite", "rumplite" (p. 9), and "kuntzite". Other spellings strike an English-speaker as strange, such as the acute accent in pricéite and wadéite. If å is used in låvenite (p. 8), why not in åkermanite?; the *umlaut* is used haphazardly in kämmererite (cf. pp. 8, 18), as is the å in låvenite (p. 32).

G. H. F.

ABELSON (PHILIP HAUGE), Editor. *Researches in Geochemistry*. New York (Wiley), 1959, x+511 pp., 73 tables; 3 pl., 127 text-figs. (1 folded insert). Price 88s.

This volume consists of the following 23 self-contained essays, based upon seminars held during 1957–8 at the Geophysical Laboratory in Washington, and at Johns Hopkins University:

Sedimentation on the ocean floor (G. O. S. Arrhenius, 24 pp.); Rates of geochemical reactions at low temperatures and pressures (R. M. Garrels, 13 pp.); Geochemical indicators of marine and freshwater sediments (M. L. Keith and E. T. Degens, 24 pp.); Geochemical prospecting (H. E. Hawkes, 17 pp.); Geochemistry of organic substances (P. H. Abelson, 25 pp.); Some chemical aspects of petroleum genesis (W. E. Hanson, 14 pp.); Mineral assemblages of the Green River formation (C. Milton and H. P. Eugster, 33 pp.); Tritium in hydrology and meteorology (W. F. Libby, 18 pp.); Measurement and use of natural radiocarbon (H. de Vries, 21 pp.); Geochronology (G. R. Tilton and G. L. Davis, 27 pp.); The variations of the O^{18}/O^{16} ratio in Nature and some geologic implications (S. Epstein, 24 pp.); Isotopic fractionation of sulfur in geochemical processes (W. U. Ault, 19 pp.); The use of equilibrium calculations in finding the composition of a magmatic gas phase (K. B. Krauskopf, 19 pp.); The chemical environment of ore deposition and the problem of low-temperature ore transport (P. B. Barton, 22 pp.); Sulfide systems as geological thermometers (G. Kullerud, 35 pp.); Some aspects of the geochemistry of carbonates (J. R. Goldsmith, 23 pp.); Diffraction effects of short-range ordering in layered sequences (F. Chayes, 18 pp.); Hydrothermal investigations of amphiboles (F. R. Boyd, 20 pp.); Reduction and oxidation in metamorphism (H. P. Eugster, 30 pp.); Local equilibrium in metasomatic processes (J. B. Thompson, 31 pp.); Activation analysis applied to geochemical problems

(G. W. Reed, 18 pp.); Chondrites and the chemical composition of the earth (G. J. F. MacDonald, 19 pp.); Equations of state and polymorphism at high pressures (S. P. Clark, 17 pp.).

The contents testify to the breadth of modern geochemical topics treated (although the Editor in his Preface stresses the limited choice imposed by considerations of space), while the list of contributors assures that each is dealt with authoritatively. The style and treatment naturally vary from essay to essay, but most are successful in presenting living pictures of their particular facets of geochemistry: the book is clearly the work of active researchers, and is unusually stimulating in drawing attention to fruitful further lines of inquiry. There are contributions to interest every geologist; tastes differ, but the reviewer found among the most fascinating: Arrhenius on sedimentation; Milton and Eugster on the bizarre mineralogy of the Green River formation; Libby on tritium; and Epstein and Ault on the isotopes of oxygen and sulphur respectively.

Emphasis is naturally on recent American work and occasionally the content of an essay may seem a little narrow in relation to its title (e.g. Reed on activation analysis); nevertheless each contribution finishes with a fairly comprehensive bibliography. The book is well printed and produced, with clear illustrations, but the omission of an index is regrettable. It is to be hoped that the present volume may turn out to be but the first of a series: there is room for such a compilation every few years, and it need not seriously overlap the Pergamon Press "Physics and Chemistry of the Earth" series. E. A. VINCENT